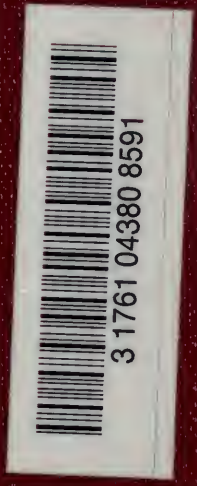

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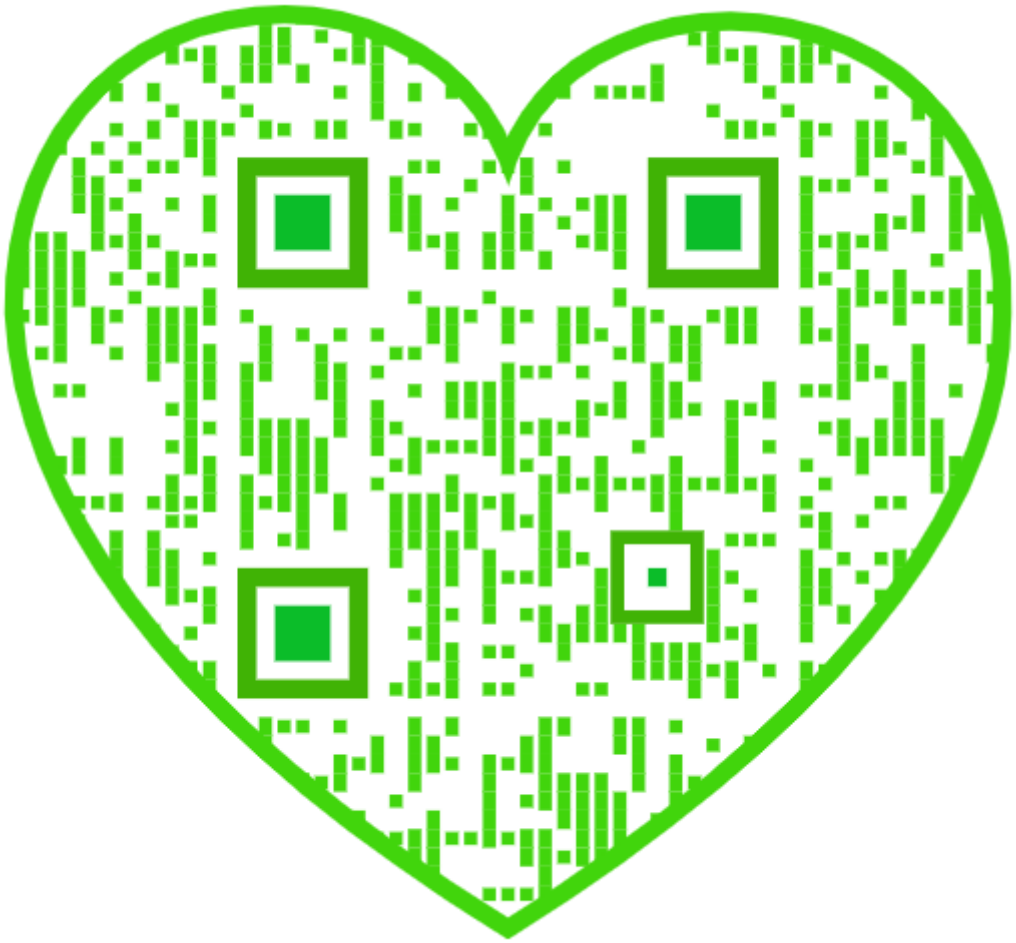

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NATURAL RESINS

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AMERICAN GUM IMPORTERS ASSOCIATION, INC.
17 Battery Place
New York, N. Y.

THE AMERICAN GUM IMPORTERS ASS'N, Inc.
360 FURMAN STREET
BROOKLYN, N. Y.

NATURAL RESINS

For a period of years, the American Gum Importers Association has been carrying on a research and development program at a large industrial laboratory. Many hundreds of varnishes have been prepared, critically examined by laboratory methods, and subjected to exposure tests. Modern formulations have been developed which meet present day demands. The results of this work are being periodically reported to the Paint and Varnish Production Clubs.

The members and the technical staff of the American Gum Importers Association will be glad to receive inquiries from manufacturers in reference to applications, varnish formulations, and uses of natural resins.

NATURAL RESINS

The use of the natural resins, either by themselves or as a constituent of coating materials for decorative and protective purposes, has been practiced from very early times. It is believed that the Egyptians used natural resins of the balsam type to varnish their mummy cases. It is probable that the natural resin was smeared on. Evidence exists that the Incas of South America employed natural resins for embalming. The properties of resins were known to the Carthaginians, the Phoenicians, and the earliest Greeks. Evidence exists in the form of varnished objects several thousands of years old and in excellent condition, that natural resins skillfully applied can yield finishes of outstanding durability. The natural lacquers, which are tree exudations, on Chinese and Japanese carriages, armor, bridges, and temples have withstood long periods of weathering in severe climates. Lacquered tableware, because of its satisfactory performance, is said to have delayed the development of porcelain.

The natural resin business is world wide in its organization, is conducted in a systematic and organized manner as far as the collection, grading, sorting, preparation for market, and distribution of the product are concerned. It is fully as well set up as a going business as is collection of rubber, the development of naval stores, the production of cocoanut and palm oil, or the preparation of sugar. The natural resin business is a stable one, ready to meet any demands made on it. It is not subject to decreasing supplies or vanishing sources of material. Its art in varnish making is old, well established, and free from patent restrictions and the attendant difficulties of such influences. The natural resins are forest products rather than synthetic materials prepared from mineral resources. As forest products they are capable of indefinite renewal.

NATURAL RESINS

The use of the natural resins was developed almost entirely in connection with the older varnish making art. Varnish making for nearly a century was hedged in by restrictions, secretiveness and close guarding of manufacturing practices. The influence of such attitude is reflected in the relatively small amount of published information on natural resins and natural resin varnishes. Some excellent texts succeeded in breaking through this veil of mystery.*

In the last decade or so this viewpoint has undergone a complete change but the natural resins still suffer from an insufficient literature. Recent publications tend to fill the gap.†

The varnish trade usually refers to the natural resins as "gums." In strict terminology, however, the gums are related to the sugars and carbohydrates. They are soluble in water, forming viscous solutions, and insoluble in drying oils and organic solvents. On heating, they decompose completely without melting. In contradistinction, the resins are insoluble in water, more or less soluble in organic substances and vegetable oils, and are chemically related to the terpenes or the essential oils. On heating the resins melt with the distillation of volatile oils terpenic in nature. The residue, termed "run" gum or resin by the varnish maker, is soluble in hot vegetable oils. Some of the softer resins are directly soluble in solvents or oils, but in all cases are totally insoluble in water.

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*Livache and McIntosh, "The Manufacture of Varnishes and Kindred Industries," Scott, Greenwood and Son, London, Vol. I, 498 pp. (1919), Vol. II, 209 pp. (1908), Vol. III, 482 pp. (1911); Coffignier, "Varnishes, Their Chemistry and Manufacture," Scott, Greenwood and Son, London, 547 pp. (1923).

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† T. Hedley Barry, "Natural Varnish Resins," Ernest Benn Limited, London, 294 pp. (1932); Barry and Dunster, "Varnish Making," Leonard Hill Limited, London, 132 pp. (1934); Robert S. Morrell, "Varnishes and Their Components," Henry Frowde and Hodder & Stoughton, London, 361 pp. (1923).

NATURAL RESINS

In general, the natural resins are divided from the point of use into those which are spirit soluble—the "spirit" originally meaning alcohol but now embracing a large variety of solvents—and those which are oil soluble. The first class is generally soluble directly, while the second needs to be processed by thermal methods. The spirit soluble resins are in general of the soft variety, while the oil soluble are usually hard. The resins are known under names which are indicative either of their source of origin, or of a distinguishing characteristic of the resin, or of the port at which they enter commerce. They are further classified into three major types: the damars, the kauris, and the copals. There is a practically continuous series as regards solubility and hardness, from the hardest copals of the fossil type to the softest damars obtained from fresh tappings of living trees.

The natural resins in general originate in the Congo district of Africa, from which the resin is named, New Zealand, the Netherlands East Indies, Malaya, the Philippine Islands, and adjacent territory. They are obtained from definite species of trees in a systematic manner, generally under governmental supervision.

NATURAL RESINS

CLASSIFICATION OF NATURAL RESINS

I. Low acid number resins, including Damar and East India type.

- A. Damar resins—spirit and oil soluble—direct acid number 25-45, m.p. 90-110° C.
  1. Batavia
  2. Singapore
- B. East India fossil or semi-fossil resins—oil soluble—indirect acid number 25-40, m.p. 125-180° C.
  1. Batu
  2. Black East India
  3. East India Singapore packing (Rasak)
  4. East India Macassar packing (Hiroe)

II. Resins of high acid number originating in the East Indies, Copal type.

- A. Manila resins
  1. Melengket or soft resins—spirit soluble—indirect acid number 135-160, m.p. 110-135° C.
  2. Loba or half hard resins—spirit soluble—indirect acid number 140-150, m.p. 110-120° C.
  3. Fossil or hard resins—spirit and oil soluble—indirect acid number 110-150, m.p. 140-165° C. Boea, Pontianak

III. African fossil or semi-fossil oil soluble—indirect acid number 110-135, m.p. 140-220° C.

- A. Congo

IV. New Zealand fossil or semi-fossil resins—spirit and oil soluble—indirect acid number 55-70, m.p. 120-160° C.

- A. Kauri
- B. Bush Kauri

ORIGIN OF NATURAL RESINS

RESIN	CLASS	TREE	MAJOR USE	COUNTRY OF ORIGIN
Boea	Copal-Fossil	Agathis Alba	Oil varnishes	Netherlands East Indies
Congo	Copal-Fossil	Copaifera	Oil varnishes	Belgian Congo, Africa
Kauri	Copal-Fossil	Agathis Australis	Oil varnishes	New Zealand
Manila	Copal	Agathis Alba	Oil and spirit varnishes	Netherlands East Indies; Philippine Is.
Pontianak	Copal	Agathis Alba	Oil and spirit varnishes	Borneo
Batavia	Damar	Hopea, Shorea	Oil and spirit varnishes	Sumatra, Borneo, Java, East Indies
Batu	Damar	Shorea	Oil varnishes	Malaya, East Indies
Black E. I.	Damar	Burseracae	Oil varnishes	Malaya, East Indies
E.I.Macassar	Damar	Dipterocarpacae	Spirit varnishes	Celebes, East Indies
E.I.Singapore	Damar	Balanocarpus	Oil and spirit varnishes	Sumatra, Borneo Malaya, East Indies

PACKAGES AND CONTAINERS

RESIN	IMPORTED FROM	PACKAGE	NET WEIGHT OF PACKAGE (Pounds)
Boea	Macassar, Netherlands East Indies	Basket bags	About 160
Congo	Antwerp, Belgium	Bags	112 and 120
Kauri	New Zealand	Cases, large	224-252
Manila	East Indian ports, Manila, P. I.	Basket bags and bags	160
Pontianak	Pontianak, Borneo, Singapore	Cases (Bold) and bags	Cases 224 Bags 160
Batavia	Batavia, Java	Cases	136
Batu	Singapore and East Indian ports	Bags	160
Black E. I.	East Indian ports, (Singapore)	Bags	160
E.I.Macassar	Macassar, Netherlands East Indies	Basket bags	175 to 200
E.I.Singapore	Singapore, Malaya	Cases	224

NATURAL RESINS

SPECIFIC GRAVITIES AND REFRACTIVE INDICES

Resin	Specific Gravity	Refractive Index
Batavia Damar Standard A/E	1.04	1.535
Batavia Damar A	1.04-1.06	1.535
Batavia Damar B	1.04-1.06	1.535
Batavia Damar C	1.04-1.06	1.535
Batavia Damar D	1.04-1.06	1.535
Batavia Damar E	1.04-1.06	1.535
Batu	1.05	1.538
Black (Damar) East India	1.04	1.541
Boea (Manila)	1.07	1.539
Congo No. 1	1.07	1.540
Congo, Ivory No. 2	1.06	1.541
East India Macassar Bold	1.03-1.04	1.543
East India Macassar Nubs	1.03	1.542
East India Macassar Chips	1.03	1.540
East India Singapore Bold	1.04	1.541
East India Singapore Nubs	1.04	1.541
East India Singapore Chips	1.03	1.540
Kauri, Brown No. 3	1.04	1.544
Kauri, Pale Chips	1.04	1.546
Kauri, Pale No. 3	1.04	1.546
Manila Loba B	1.07	1.539
Manila Loba C	1.07	1.540
Manila Loba D	1.08	1.539
Manila Loba DK	1.07	1.538
Manila Loba CNE	1.07	1.538
Manila WS	1.06	1.526
Manila MA	1.06	1.526
Manila CBB	1.07	1.538
Manila DBB	1.06	1.538
Pontianak (Copal) Nubs	1.07	1.540
Sandarac	1.05	1.545
Singapore Damar No. 1	1.05	1.538

NATURAL RESINS

COMMERCIAL GRADES OF NATURAL RESINS

SINGAPORE DAMAR GUMS

Singapore Damar No. 1
Singapore Damar No. 2
Singapore Damar No. 3
Singapore Damar Chips
Singapore Damar Seeds
Singapore Damar Dust

PALE EAST INDIA GUMS (Singapore Packing)

Pale East India Bold
Pale East India Nubs
Pale East India Chips
Pale East India Dust

PALE EAST INDIA GUMS (Macassar Packing)

Pale East India Bold—Hiroe
Pale East India Nubs—Hiroe
Pale East India Chips—Hiroe
Pale East India Dust—Hiroe

The gradings of Singapore Damar are on the basis of color and freedom from impurities, the number 1 being the lightest or most nearly white. This grade is translucent but almost transparent. Numbers 2 and 3 are less transparent and have some color. The designations Chips Seeds, and Dust are primarily size classifications, but decreasing size usually carries with it increasing amounts of impurities.

The Pale East India gums of Singapore packing are dark red or brownish in color. They are sometimes termed Rasak. The Pale East India gum of Macassar packing, often called Hiroe, is usually reddish yellow and paler than those of Singapore packing. The East India gums of Macassar packing contain more wax than the Pale East India Singapore.

The Bold designation refers to size of pieces—that is, large and clean. The Nubs are smaller, of the order of 2 to 4 cm. in largest dimension. Chips, Seeds, and Dust are size and quality gradings analogous to those of Singapore Damar.

NATURAL RESINS

COMMERCIAL GRADES OF NATURAL RESINS

BATAVIA DAMAR GUMS

Batavia Damar A/E Standard
Batavia Damar A/D Mixed
Batavia Damar "A"
Batavia Damar "B"
Batavia Damar "C"
Batavia Damar "D"
Batavia Damar "E"
Batavia Damar "F"
Batavia Damar Dust

The letter designations of Batavia Damar are primarily size classifications and secondarily those of color and impurities, the amount of which usually increase with decreasing size. The grades refer to the material retained on the specified screens as given below. The A material is that retained on an A screen; B material, that which is through the A screen and retained on the B; C material is that which passes through the B screen and is held back by the C screen; D material, in a similar manner, that which passes through the C screen and is retained on the D; an E material, often known as Seeds, that which passes through the D screen and is retained on the E sieve, while an F material and Dust are products passing through the E screen. The F grade is dirtier than E and is composed of splinters rather than seeds.

SIEVES USED IN PREPARING STANDARD QUALITIES OF BATAVIA GUM DAMAR

A—Sieve of gauze with six-cornered holes about 15mm. (38/64 in. or .59 in.) long and broad, made of wire Birmingham Wire Gauge size 21, or .032 in. diameter.

B—Sieve of iron gauze, 3 square holes per inch, made of wire Birmingham Wire Gauge size 17, or .058 in. diameter.

C—Sieve of iron gauze, 6 square holes per inch, made of wire Birmingham Wire Gauge size 19, or .042 in. diameter.

D—Sieve of iron gauze, 11 square holes per inch, made of wire Birmingham Wire Guage size 23, or .025 in. diameter

E—Sieve of yellow copper gauze, 40 square holes per inch, made of wire Birmingham Wire Gauge size 30, or .012 in. diameter.

NATURAL RESINS

COMMERCIAL GRADES OF NATURAL RESINS

BATU EAST INDIA GUMS

Batu Scraped
Batu Unscraped
Batu Nubs and Chips
Batu Chips
Batu Dust

BLACK EAST INDIA GUMS

Black Bold Scraped
Black Bold Unscraped
Black Nubs and Chips

The Batus and Black East India gums are both Damars. The Batu is opaque and usually quite light in color, being predominantly yellow. Batu when fresh is usually of a dark brown color which bleaches with age to a light yellow. The Black East India is very dark, almost black. This material is known among the natives as Damar Hitam or Black Damar. Black East India varnishes when applied to surfaces bleach and become very much lighter in color.

The term Bold is a size classification, referring to large pieces which are either scraped by hand with a knife to remove surface coatings, crusty material, or oxidized resin, or unscraped, a designation which refers to original pieces after sorting and preliminary cleaning. Nubs and Chips are materials of smaller size, either occurring naturally or as the result of cleaning, while the terms Chips and Dust mean the same as heretofore stated.

NATURAL RESINS

PONTIANAK GUMS

Pontianak Bold Scraped
Pontianak Mixed Bold
Pontianak Cuttings
Pontianak Nubs
Pontianak Chips

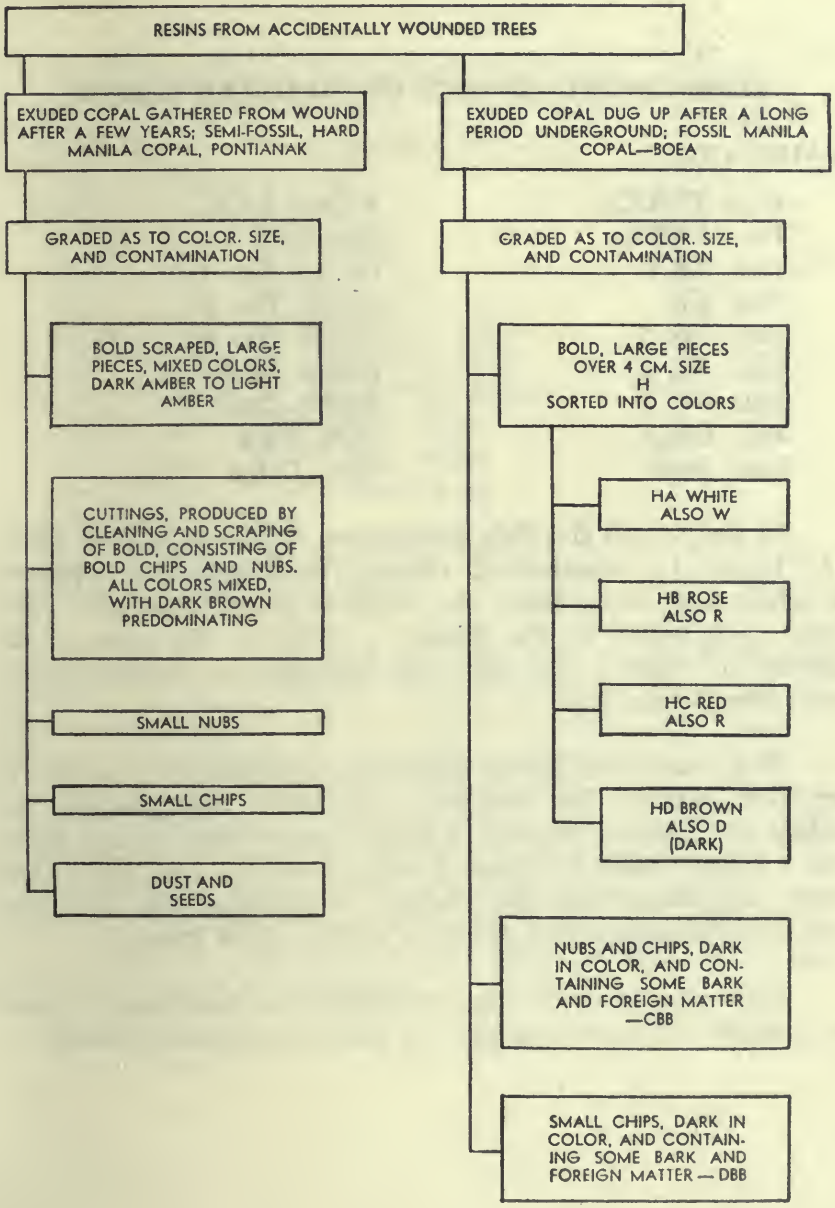
BOEA (MANILA FOSSIL) GUMS

Hard Bold White
Hard Bold Amber
Hard Bold Dark

Pontianak is one of the Manila gums from Agathis Alba. The Bold Scraped is characterized by being harder than the Mixed Bold which is quite hard but of varying colors. The Cuttings are large chips resulting from cleaning or breaking down Bold pieces. Nubs and Chips are size classifications as before. Pontianak is a semi-fossil hard Manila copal. It is exuded resin which has hardened over a period of several years. Exudations ordinarily result from accidental wounding of the trees.

Boea is a fossil Manila resin. It is exuded copal resin dug up after a long period underground. It is of the same order of hardness as Pontianak.

MANILA RESINS FROM AGATHIS ALBA OIL AND SPIRIT SOLUBLE


RESINS FROM ACCIDENTALLY WOUNDED TREES
EXUDED COPAL GATHERED FROM WOUND AFTER A FEW YEARS; SEMI-FOSSIL, HARD MANILA COPAL, PONTIANAK
EXUDED COPAL DUG UP AFTER A LONG PERIOD UNDERGROUND; FOSSIL MANILA COPAL—BOEA
GRADED AS TO COLOR. SIZE, AND CONTAMINATION
GRADED AS TO COLOR. SIZE, AND CONTAMINATION
BOLD SCRAPED, LARGE PIECES, MIXED COLORS, DARK AMBER TO LIGHT AMBER
CUTTINGS, PRODUCED BY CLEANING AND SCRAPING OF BOLD, CONSISTING OF BOLD CHIPS AND NUBS. ALL COLORS MIXED, WITH DARK BROWN PREDOMINATING
SMALL NUBS
SMALL CHIPS
DUST AND SEEDS
BOLD, LARGE PIECES OVER 4 CM. SIZE H SORTED INTO COLORS
HA WHITE ALSO W
HB ROSE ALSO R
HC RED ALSO R
HD BROWN ALSO D (DARK)
NUBS AND CHIPS, DARK IN COLOR, AND CONTAINING SOME BARK AND FOREIGN MATTER —CBB
SMALL CHIPS, DARK IN COLOR, AND CONTAINING SOME BARK AND FOREIGN MATTER — DBB

COMMERCIAL GRADES OF NATURAL RESINS

KAURI GUMS

Pale XXXXX	Brown XXX
Pale XXXX	Brown X
Pale XXX	Brown No. 1
Pale XX	Brown No. 2
Pale No. 1	Brown No. 3
Pale No. 2	Brown Chips
Pale No. 3	Brown Dust
Pale Chips	Bush Bold
Pale Dust	Bush Chips

In the Kauris the Pale designation refers to lack of color. The higher the number of crosses, the closer the approach to white and the greater the freedom from impurities. The cross designation in the Brown is similar: the greater the number of crosses, the closer the approach to complete freedom from impurities.

In general, the Kauri gums are partially transparent in the Pale grades. The number 1, 2, and 3 designations are orders of hardness, number 1 being harder than 2, and number 2 harder than 3. These grades, however, are lower than those designated with the crosses. The Chips and Dust are size classifications, as in the case of the other gums.

Bush gum is virgin material which has fossilized in place on branches of trees and has not been found underground.

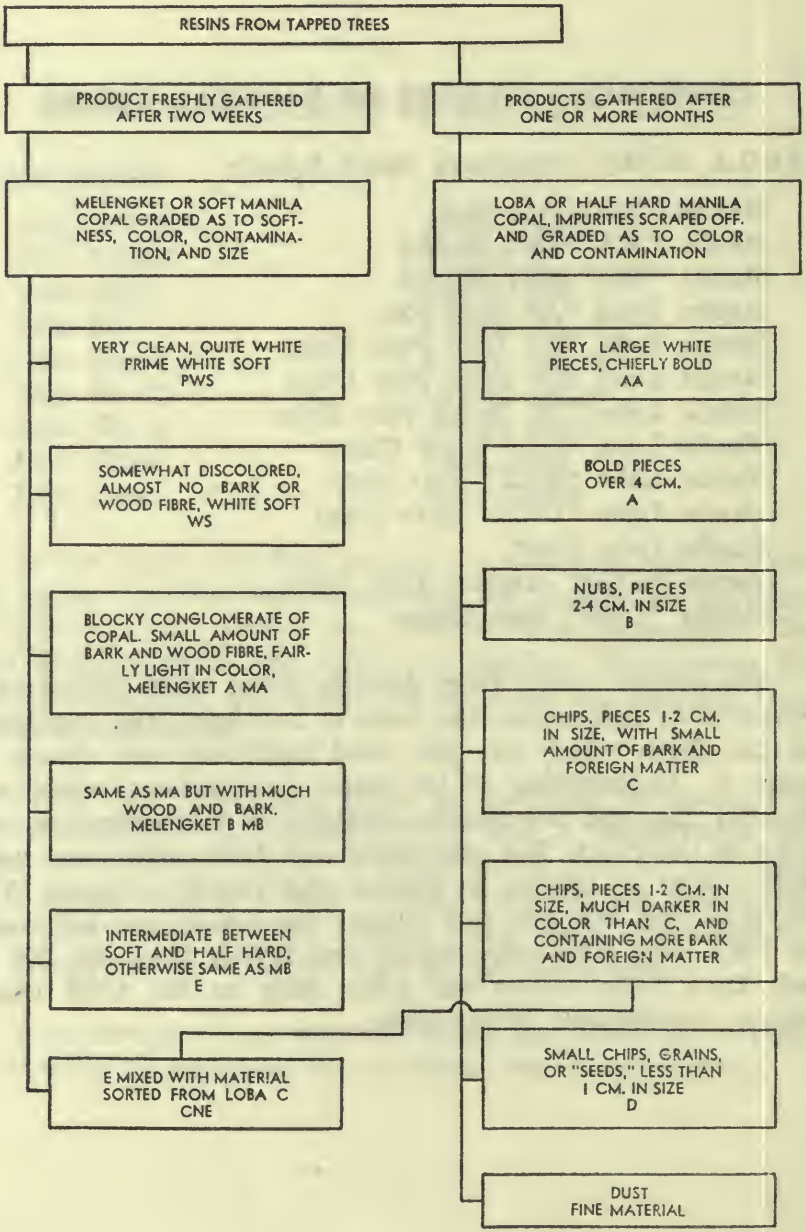
COMMERCIAL GRADES OF NATURAL RESINS

MANILA GUMS (Macassar) Spirit Soluble

Manila "WS" Pale Soft
Manila "MA" Soft Blocky
Manila "MB" Soft Blocky
Manila Loba "A" Bold Pale
Manila Loba "B" Bold Pale Nubs
Manila Loba "C" Bold Pale Chips
Manila Loba "D" Small Pale Chips
Manila Loba "DK" Dark Chips
Manila Loba "FAX" Pale Nubs
Manila Loba "CNE" Dark Nubs
Manila Loba Dust
Manila "CBB" Medium Pale Nubs
Manila "DBB" Pale Chips

The manila resins from Agathis Alba, which include the Melengket or soft resins, the Loba or half-hard, the Pontianak and the Boea which are the hard materials, are shown in Figure 1. Descriptions of the letter designations, which are primarily size and secondarily amounts of contamination, are shown in the chart. The Melengket and Loba resins are spirit soluble—that is, soluble in alcohol and related solvents. The WS, MA, and MB are soft resins; the Lobas are half-hard. The FAX Pale Nubs are cleaner and lighter than the DK or small Dark Chips which are quite dirty or the CNE which contains considerable crusty gum.

MANILA RESINS FROM AGATHIS ALBA SPIRIT SOLUBLE


RESINS FROM TAPPED TREES
PRODUCT FRESHLY GATHERED AFTER TWO WEEKS
PRODUCTS GATHERED AFTER ONE OR MORE MONTHS
MELENGKET OR SOFT MANILA COPAL GRADED AS TO SOFTNESS, COLOR, CONTAMINATION, AND SIZE
LOBA OR HALF HARD MANILA COPAL, IMPURITIES SCRAPED OFF. AND GRADED AS TO COLOR AND CONTAMINATION
VERY CLEAN, QUITE WHITE PRIME WHITE SOFT PWS
SOMEWHAT DISCOLORED, ALMOST NO BARK OR WOOD FIBRE, WHITE SOFT WS
BLOCKY CONGLOMERATE OF COPAL. SMALL AMOUNT OF BARK AND WOOD FIBRE, FAIRLY LIGHT IN COLOR, MELENGKET A MA
SAME AS MA BUT WITH MUCH WOOD AND BARK. MELENGKET B MB
INTERMEDIATE BETWEEN SOFT AND HALF HARD, OTHERWISE SAME AS MB E
E MIXED WITH MATERIAL SORTED FROM LOBA C CNE
VERY LARGE WHITE PIECES, CHIEFLY BOLD AA
BOLD PIECES OVER 4 CM. A
NUBS, PIECES 2-4 CM. IN SIZE B
CHIPS, PIECES 1-2 CM. IN SIZE, WITH SMALL AMOUNT OF BARK AND FOREIGN MATTER C
CHIPS, PIECES 1-2 CM. IN SIZE, MUCH DARKER IN COLOR THAN C, AND CONTAINING MORE BARK AND FOREIGN MATTER
SMALL CHIPS, GRAINS, OR "SEEDS," LESS THAN 1 CM. IN SIZE D
DUST FINE MATERIAL

COMMERCIAL GRADES OF NATURAL RESINS

MANILA GUMS (Philippine) Spirit Soluble

- Manila Extra Bold Pale Scraped
- Manila Bold Pale
- Manila Bold Extra Pale Sorts
- Manila Bold Pale Chips
- Manila Pale Small Chips
- Manila Bold Amber Sorts
- Manila Seeds and Dust

Philippine Manila gums are obtained from the Philippine Islands and are spirit soluble. They are similar in character to the Loba gums. The gradings are according to color, cleanliness, and size.

SINGAPORE MANILA GUMS

- White Split Chips
- Singapore Manila Dust

NATURAL RESINS

COMMERCIAL GRADES OF NATURAL RESINS

VARIOUS GUMS

Gum Elemi
Gum Mastic
Red Gum Coarse
Red Gum Powdered
Sandarac Gum

Gum Elemi is the soft colorless or white resin obtained from the tree *canarium indicum* in the Philippines. It is soluble in a number of organic solvents such as alcohol ether, and chloroform. It finds application in the manufacture of paints, varnishes, lacquers, inks, linoleum, and in a number of process industries.

Mastic is produced by the tree *pistacia lentiscus*. It is mainly collected on the island of Chios, east of the Grecian mainland. It is often employed in the manufacture of high grade varnishes of very pale color for the protection of pictures in oils and watercolors. The common solvents are alcohol or turpentine.

Red gum is also known as gum Accroides or Grass Tree gum. It is derived from various species of *xanthorrhoea*. Its main use is in the manufacture of spirit varnishes.

Sandarac is obtained from coniferous trees of the species *tetraclinis*. It is used for the manufacture of white hard spirit varnishes for labels, cardboard, leather, wood, and metals.

COMMERCIAL GRADES OF NATURAL RESINS

CONGO GUMS

White and Ivory Gums

No. 1 Water White Transparent
2 Cloudy White
14 Selected Fully Scraped Ivory
15 Ordinary Ivory Sorts
16 Inferior Ivory Sorts
24 No. 1 Ivory Nubs
25 No. 2 Natural Ivory Nubs

Straw Colored Congo Gums

No. 3 Selected Pale Straw Bold
4 Pale Bold Straw
5 Pale Bold Straw
7 Pale Straw Bold Washed
18 Pale Straw Nubs
19 Pale Straw Nubs

Pale Congo Gums

No. 17 No. 1 Pale Fingers
26 Bold Pale Chips
27 Small Pale Chips
28 Pale Dust

Amber Congo Gums

No. 6 Pale Amber Bold
8 Light Amber Bold
9 Medium Light Amber Bold
10 Rescraped Hard Dark Amber
11 Hard Dark Amber Bold
20 Dark Hard Amber Nubs

Sorts and Selections of Congo Gums

No. 12 Selected Sorts Bold
13 Dark Sorts Bold
21 Selected Nubs Ordinary
22 Small Mixed Nubs
23 Dark Mixed Nubs

NATURAL RESINS

The Congos may be classified as to color into grades known as White and Ivory, Straw and Pale, which are slightly darker than White, Amber of both the pale and dark varieties, as well as mixed designations such as Sorts. The individual resins also carry hardness designations as well as names indicating surface conditions such as "Fully Scraped," "Rescraped," or treatment during sorting such as "Washed." The terms Bold, Nubs, Chips, and Dust are size classifications as in the case of the other gums. Sorts are grades of a number of colors, while fingers indicate a shape which is similar to that of the human finger. The number opposite each one of the designations is the standard American Gum Importers' classification number. All members of the Association use this designation, although often the same grade of gum may be known to the trade by a number of other identifications as well as the American Gum Importers' Congo number.

PROPERTIES OF NATURAL RESINS

In the following tables of properties of the natural resins, an arbitrary classification is made into those which are oil soluble and those which are spirit soluble. The term "oil soluble" is perhaps slightly misleading, inasmuch as the resins are compatible with drying oils usually only after running. The term "spirit soluble" in its original designation meant alcohol soluble, but is here extended to mean soluble in organic solvents. A number of resins, such as the Congos, are neither oil nor spirit soluble in their original condition, but after running show spirit solubility.

The direct acid number refers to a determination in which the resin in a suitable solvent is titrated directly with a standard alkali and the acid number reported in equivalent milligrams of potassium hydroxide per gram of resin. The indirect acid number is determined by a method in which a relatively large amount of alkali, more than necessary to satisfy all of the acids in the resin, is reacted with a definite weight of the resin and the excess alkali determined by titration with a standard acid. The acid number is calculated as in the direct method. Usually the indirect acid number is higher than that determined directly. The divergences are not as marked in the case of the Batavia Damars as in some of the other resins.

Softening point was determined by the capillary tube method. The melting points have been determined by the mercury method of Durran, as modified by Rangaswami and reported in the Journal of the Oil and Color Chemists Association, 1930, Volume 13, page 287. This method gives definite results that could be closely duplicated. Determination of melting point by the cube method does not give closely duplicatable results nor results which agree with those obtained by the mercury method. The values given in the table for acid numbers, softening point, and melting point are only median figures and not absolute ones. Commercial materials will show divergences of either a plus or minus nature from the median values given in the tables.

PROPERTIES OF NATURAL RESINS
Oil Soluble

Natural Resin	Percent Moisture	Direct Acid Number	Indirect Acid Number	Softening Point Deg. C.	Melting Point Deg. C.
Batu, Bold Scraped	3	18	33	132	180
Black E. I. Bold Scraped (Damar Hitam)	1.5	20	36	125	164
Boea, Medium Dark	2.9	126	149	115	148
Congo, Hard Dark Amber (No. 11)	0.7	102	123	104	200
Congo, Ivory Rescraped (No. 14)	1.8	92	111	91	144
Congo, Medium Pale (No. 9)	0.4	110	132	85	220
Damar, Standard Batavia	1.2	26	32	85	108
E. I. Singapore, Pale Bold	0.7	20	37	128	156
Kauri, No. 1 Brown	5.4	57	67	120	152
Pontianak, Genuine Bold	3.4	113	122	135	161
Pontianak, Nubs	3.1	118	126	135	169
Pontianak, Small Chips	3.3	120	127	132	156

PROPERTIES OF NATURAL RESINS
SPIRIT SOLUBLE

Resin	Direct Acid Number	Indirect Acid Number	Softening Point, Deg. C.	Melting Point, Deg. C.	Iodine Number
Batavia Damar, Standard A/E.....	31	34	76	102	95
Batavia Damar A.....	26-28	26-30	65-75	96-99	96-100
Batavia Damar B.....	24-30	24-31	67-75	99-100	95-96
Batavia Damar C.....	22-32	24-33	70-75	99-100	96
Batavia Damar D.....	25-32	28-34	72-75	99-100	89-93
Batavia Damar E.....	27-33	33-39	74-75	99-102	79-84
Batavia Damar Dust.....	32	44	76	102	64

Values given are median. Individual batches will vary somewhat from these values.

PROPERTIES OF NATURAL RESINS
SPIRIT SOLUBLE

Resin	Direct Acid Number	Indirect Acid Number	Softening Point, Deg. C.	Melting Point, Deg. C.	Iodine Number
East India (Macassar) Bold.....	16-20	23-30	101-109	127-156	97-115
East India (Macassar) Nubs....	20-22	28-32	103-107	127-143	66-85
East India (Macassar) Chips....	24	37	120	133	84
East India (Macassar) Dust.....	28	46	122	140	80
East India (Singapore) Bold.....	19	26	110	140	83
East India (Singapore) Nubs...	19	28	110	163	81
East India (Singapore) Chips..	23	33	110	138	87
East India (Singapore) Dust....	27	43	114	150	81
Manila Loba B.....	136	147	90	120	116
Manila Loba C.....	141	155	88	114	119
Manila Loba D.....	127	151	89	114	115
Manila Loba DK.....	127	146	89	114	107
Manila Loba CNE.....	125	144	90	116	130
Manila Loba Dust.....	110	134	91	116	68
Manila WS.....	130	145	88	115	145
Manila MA.....	130	150	90	115	130
Manila CBB.....	141	151	90	119	114
Manila DBB.....	140	154	88	120	113

Values given are median. Individual batches will vary somewhat from these values.

SOLUBILITY OF MANILA AND DAMAR RESINS

Resin	Acetic Acid, Glacial	Acetone	Acetylene Tetrachloride	Alcohol, Denatured No. 1	Alcohol Denatured No. 5 (Pyro)	Amyl Acetate
Batavia Damar, Standard A/E	i	i	S	i	i	Sx
Batavia Damar, E Seeds	i	i	S	i	i	Sx
Batavia Damar, Dust	i	i	S	i	i	Sx
Manila Loba B	is	S	s	S	S	S
Manila Loba C	is	S	S	Sx	Sx	S
Manila Loba D	is	S	s	S	S	S
Manila Loba DK	is	S	s	S	S	S
Manila Loba CNE	is	S	s	S	S	S
Manila Loba Dust	is	S	is	S	S	S
Manila WS	is	S	S	Sx	Sx	S
Manila MA	is	S	S	Sx	Sx	S
Manila CBB	is	S	S	Sx	Sx	S
Manila DBB	is	S	S	Sx	Sx	S
East India (Macassar) Bold	i	i	S	i	i	i
East India (Macassar) Nubs	i	i	S	i	i	i
East India (Singapore) Bold	i	i	S	i	i	s

S=Soluble
Sx=Soluble, cloudy solution
s=Largely soluble
is=Partly soluble
i=Slightly soluble
I=Insoluble

SOLUBILITY OF MANILA AND DAMAR RESINS

Resin	Ansol	Benzol	Butyl Alcohol Normal	Carbon Tetrachloride	Cellosolve	Cellosolve Acetate
Batavia Damar, Standard A/E	i	S	i	S	i	i
Batavia Damar, E Seeds	i	S	i	S	i	i
Batavia Damar, Dust	i	S	i	S	i	i
Manila Loba B	S	is	S	s	S	S
Manila Loba C	Sx	is	s	s	S	S
Manila Loba D	S	is	S	s	S	S
Manila Loba DK	S	is	S	s	S	S
Manila Loba CNE	S	is	S	s	S	S
Manila Loba Dust	S	is	S	s	S	S
Manila WS	Sx	is	s	s	S	S
Manila MA	Sx	is	s	s	S	S
Manila CBB	Sx	is	s	s	S	S
Manila DBB	Sx	is	s	s	S	S
East India (Macassar) Bold	i	Sx	i	S	i	i
East India (Macassar) Nubs	i	Sx	i	S	i	i
East India (Singapore) Bold	i	S	i	S	i	i

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SOLUBILITY OF MANILA AND DAMAR RESINS

Resin	Chlorbenzol	Dichloro Ethyl Ether	Dipentene	Ethyl Acetate	Ethyl Ether	Ethylene Dichloride
Batavia Damar, Standard A/E	S	i	S	i	Sx	Sx
Batavia Damar, E Seeds	S	i	S	i	Sx	Sx
Batavia Damar, Dust	S	i	S	i	Sx	Sx
Manila Loba B	s	s	is	S	S	s
Manila Loba C	s	is	I	S	s	s
Manila Loba D	s	is	i	S	S	is
Manila Loba DK	s	is	i	S	S	is
Manila Loba CNE	s	is	i	S	S	is
Manila Loba Dust	s	is	i	S	S	s
Manila WS	is	i	I	S	s	s
Manila MA	is	s	I	S	s	s
Manila CBB	s	is	I	S	s	s
Manila DBB	s	is	I	S	s	s
East India (Macassar) Bold	S	i	Sx	i	Sx	Sx
East India (Macassar) Nubs	Sx	i	Sx	i	Sx	Sx
East India (Singapore) Bold	S	i	S	i	s	Sx

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Sx=Soluble, cloudy solution
s=Largely soluble
is=Partly soluble
i=Slightly soluble
I=Insoluble

SOLUBILITY OF MANILA AND DAMAR RESINS

Resin	Isopropyl Alcohol	Isopropyl Ether	Kerosene	Linoleic Acid	Methyl Alcohol	Tetralin
Batavia Damar, Standard A/E	i	Sx	S	s	i	S
Batavia Damar, E Seeds	i	Sx	S	s	i	S
Batavia Damar, Dust	i	Sx	S	s	i	S
Manila Loba B	S	is	I	s	Sx	is
Manila Loba C	S	is	I	s	Sx	i
Manila Loba D	S	is	I	s	Sx	i
Manila Loba DK	S	is	I	s	Sx	i
Manila Loba CNE	S	is	I	s	Sx	is
Manila Loba Dust	S	is	I	s	Sx	is
Manila WS	S	is	I	s	Sx	i
Manila MA	S	is	I	s	Sx	i
Manila CBB	S	is	I	s	Sx	i
Manila DBB	S	is	I	s	Sx	i
East India (Macassar) Bold	i	Sx	S	s	i	S
East India (Macassar) Nubs	i	Sx	S	s	i	S
East India (Singapore) Bold	i	is	S	s	i	S

S=Soluble
Sx=Soluble, cloudy solution
s=Largely soluble
is=Partly soluble
i=Slightly soluble
I=Insoluble

SOLUBILITY OF MANILA AND DAMAR RESINS

Resin	Toluol	Turpentine	Varnolene
Batavia Damar, Standard A/E	S	S	S
Batavia Damar, E Seeds	S	S	S
Batavia Damar, Dust	S	S	S
Manila Loba B	is	I	I
Manila Loba C	is	I	I
Manila Loba D	is	I	I
Manila Loba DK	is	I	I
Manila Loba CNE	is	I	I
Manila Loba Dust	is	I	I
Manila WS	is	I	I
Manila MA	is	I	I
Manila CBB	is	I	I
Manila DBB	is	I	I
East India (Macassar) Bold	Sx	Sx	Sx
East India (Macassar) Nubs	Sx	Sx	Sx
East India (Singapore) Bold	S	S	S

S=Soluble
Sx=Soluble, cloudy solution
s=Largely soluble
is=Partly soluble
i=Slightly soluble
I=Insoluble

NATURAL RESINS

PROPERTIES OF RUN GUMS

Resin	Estimated % Loss in Weight on Running	Direct Acid Number After Running	Softening Point Deg. C.	Melting Point Deg. C.
Batu, Bold Scraped.....	15	15	120	135
Black, E. I. Bold Scraped (Damar Hitam)	15	17	125	145
Boea, Medium Dark.....	20	95	105	125
Congo, Hard Dark Amber (No. 11)	20	78	90	125
Congo, Ivory Rescraped (No. 14)	15	92	90	105
Congo, Medium Pale (No. 9)	20	70	110	120
Damar, Standard Batavia	10	17	100	110
E. I. Macassar, Bold.....	13	17		165
E. I. Macassar, Nubs.....	11	17		144
E. I. Macassar, Dust.....	11	15		128
E. I. Singapore, Bold.....	15	9	120	135
E. I. Singapore, Nubs.....	10	14		148
E. I. Singapore, Dust.....	13	16		142
Kauri, No. 1 Brown.....	25	35	80	105
Macassar (Manila) MA....	30	45	105	110
Manila, DBB Soluble Chips	30	97	90	140
Manila Loba B.....	30	59	105	130
Pontianak, Genuine Bold..	20	95	125	130

NATURAL RESINS

Research on Natural Resins and Their Uses

The first work undertaken has been a study of the varnish making properties and values of natural resins and a comparison of them with competitive products. In the course of this work a large number of varnishes have been made and studied.

Other work planned and under way consists of a study of special formulations for the better use of the natural resins and of methods of modifying them in ways to improve their varnish making properties and the ease of using them.

The appearance of synthetic resins on the market while China wood oil was still a very new product and the large use made of it in synthetic resin formulae make it highly probable that synthetic resins have received credit for many of the values that properly belong to China wood oil. Certainly when quick drying varnishes and enamels became prominent they were generally credited to synthetic resins, whereas it is well known that natural resins with China wood oil also give quick drying results. With these considerations in mind, the varnishes we have prepared and studied have contained high percentages of China wood oil.

Preparation of Varnishes and Laboratory Tests on Them

One of the purposes of the research program of the American Gum Importers Association is to demonstrate the excellent values and properties of the natural resins and to publish this information to the trade.

To accomplish this, several hundred varnishes have been made and their properties determined by numerous laboratory tests and by weathering. In preparing these varnishes care has been taken to formulate and cook them under conditions as nearly identical as are practical and both natural and synthetic resins have been used, to permit a comparison of their properties.

Varnish Cooking

One-gallon lots of the varnishes were cooked in heavy copper kettles. The removable lids of these pots, in addition to thermometer hole, funnel hole for adding oil and a large stirring hole with a removable cover, were fitted on the under side with a drip ring which returned the condensed liquids directly into the kettle without running down its superheated sides.

NATURAL RESINS

The natural resins were run in the customary way and then the China wood oil, heated to 400°F., was added and the varnish cooked at 560°F. until the desired body was reached. The bodied linseed was then added as a check oil and the batch thinned.

The synthetic resin varnishes were each cooked by the methods recommended by their manufacturers, then checked and thinned. Many of these cooks—except for running the resin—were the same as those described for the natural resins. These varnishes are identical except for the resin used, and therefore make possible comparisons of the relative values and properties of each resin in varnishes of this type of formula.

After aging for a week or more the varnishes were centrifuged.

Driers

Soluble type driers were added after centrifuging. The ratio of metals used has been chosen to give a balanced drier capable of a wide variety of uses. The ratio of lead to cobalt is about 45:1 to give through drying with a minimum of top drying and risk of destructive action. The quantity used has been kept low and is less than that recommended for a number of prominent synthetic resin spar varnishes. 0.4% Lead, 0.03% manganese and 0.0088% cobalt calculated as metals and based on the drying oil content of the varnishes were used.

Preparation of Panels

The selected maple and redwood panels 5"x10"x1", prepared from seasoned lumber, were stored in the laboratory several weeks before using. The 5"x10" metal panels were 20 gauge, "single pickle," automobile sheet steel. These 5"x10" panels were used for weathering tests and 3"x5" 24 gauge steel and 31 gauge tin panels were used for the laboratory tests.

The metal panels were washed twice with benzol and sanded with No. 7/0 wet or dry sandpaper before varnishing. For the wooden panels "00" paper was used.

The varnishes were brushed on in a routine manner by one operator, taking care to have each as similar as possible.

After three days the panels were sanded with "00" sandpaper and a second coat of varnish applied. One week after the final coat the panels were put on the weather test rack.

One coat of varnish was applied to the 3"x5" panels for laboratory tests, two coats to the 5"x10" metal panels and three to the wood panels for weathering.

Laboratory Tests of Varnishes

The determination of dust-free and tack-free drying rates was made by the usual finger-touch method. A varnish was considered tack free when the observer could press his thumb hard against it and, when withdrawing it, discover no feeling of tackiness.

Viscosity was determined by reference to the Gardner-Holdt bubble test standards and color by comparison with the Gardner color standards.

Relative hardness was determined after twenty-four hours, seventy-two hours and seven days drying. As only relative figures were required, the simple lead pencil test was used as follows: A set of Venus pencils from "H" to "9 H" was pointed in a mechanical pencil sharpener. A pencil of suitable hardness held vertical to the varnished metal was pushed against the film. If the point crumbled a harder pencil was tried until the softest pencil which would just pierce the film was selected. Proof of piercing the film was given by dragging the point a short distance through the film, exposing the metal below. The "H" number of this pencil was recorded as the hardness of the film, the larger numbers indicating greater hardness. Pencils were repointed after each determination.

Relative gloss was determined by examining the reflected image of a standard optician's eye testing chart and determination of the finest line of print which could be read under standard conditions. A chart having reversed characters was prepared by photographing the original on film and making a mirror image black on white enlargement of it the same size as the original. The letters in line No. 1 were 3¼" and those in line No. 11 were 5/32" high. This chart was mounted at eye-level height opposite a window giving clear diffused light, with the varnished panel to be tested placed five feet in front of the chart and slightly to one side. The number of the finest line which could be clearly read was recorded as the relative gloss. The varnished panels used in this test had a baked white undercoat.

The cold water test was made by immersing half the length of a 3"x5" panel in cold distilled water for four days. The boiling water and boiling 5% Ivory soap tests were run for one hour in a similar manner.

The gas proofness was determined by the method of the Bureau of Standards for interior varnishes. Panels which had dried for one-fifth, two-fifths, three-fifths and four-fifths of the time required for them to set to touch were placed in a bell jar with a kerosene lamp which burned until it went out. If the slightest trace of crystalization or frosting was observed on any panel the varnish was listed as not gas-proof.

The kauri reduction number was determined by the method described in the United States Government Master Specifications for spar varnish. It was carried out to an accuracy of 10 in the final number and the appearance of a *single* fine crack in the bending test was considered as a failure.

Weathering the Varnishes

All of the varnishes were weathered on the 5"x10" steel, maple and redwood panels. These were exposed on a large test rack at the Hilton-Davis Company, at Cincinnati. This rack is 165 feet long and holds 550 lineal feet of panels 5" wide. It is in a semi-industrial location, with an active railroad and two factories within 800 feet. The panels are mounted at a 45" angle facing south. Every four weeks the panels are examined with the aid of a small hand lens.

Photomicrographs

When each group of varnishes had weathered long enough for fairly extensive failure to develop, 10 diameter photomicrographs were made from the ones of greatest interest. This permanent record of their condition serves as a check on the weather test reports and has also been very useful for making comparisons between them.

Varnishes Containing Only One Resin

The first varnishes made were a group of about 100, each of which contained only one resin.

In many cases two or more varnishes of the same composition were made having different methods of cooking, different viscosities, etc.

A group of control varnishes for comparison with the natural resin varnishes was made from ester gum and concentrated and modified synthetic resins.

Eight "All Purpose," floor and spar type varnishes were purchased at paint and hardware stores and also used for controls.

Fifteen, 25 and 50 gallon varnishes were made from most of the resins used. From some of them separate groups of varnishes were made in which the oils were 75%, 90% or 100% China wood oil and the remainder was bodied linseed.

The formulation for each group of varnishes was identical except as to the resin used.

A Typical 25-Gallon Formula

400 parts Hard Dark Amber Congo (No. 11)

680 parts China wood oil

120 parts 4-hour linseed oil

960 parts Varnolene

240 parts Hi-Flash naphtha

All varnishes contain 50% non-volatile. The higher solvency thinners were used in all of the varnishes because some of the resins required them.

PHYSICAL PROPERTIES OF SINGLE RESIN 50-GALLON VARNISHES

No.	Resins	Per cent CWO	Kauri Number	Relative Gloss	Gas Proofness	Hours till tack free	Viscosity	Relative Hardness after 7 days	Loss of gloss or softening after 1 hr. boiling water	1 hr. in 5% Ivory Soap	4 days in water
2042	No. 1 Brown Kauri	90	150	3	OK	2	B	4	OK	Mo	Mo
2041	Genuine Bold Pontianak	90	150	6	F	2	C	4	OK	VM	Mo
2051	Bold Black Scraped	90	150	3	OK	2½	C	3	OK	OK	Mo
2044	Pale Bold East India	90	130	4	OK	2½	E	5	OK	VM	Mo
2052	Manila DBB Chips	75	160	3	OK	2	D	2	OK	VM	Mo
2055	Boea Medium Dark	75	150	4	F	2	G	4	OK	M	Mo
2043	Batu Bold Scraped	90	130	5	OK	4	D	4	OK	Mo	Mo
1003	Concentrated Phenolic No. 1	100	200	2	OK	2	H	5	OK	Mo	Mo
1007	Modified Phenolic No. 4	90	150	6	OK	3	B	4	OK	M	Mo
1009	Modified Phenolic No. 5	90	150	4	F	2	C	3	OK	M	Mo
1010	Modified Phenolic No. 6	90	130	7	OK	2½	B	4	OK	VM	Mo
501	Commercial Spar No. 1	....	110	6	F	5	G	2	OK	VM	OK
502	Commercial Spar No. 2	....	60	4	OK	5	D	3	OK	VM	Mo
505	Commercial Spar No. 5	....	150	9	OK	5	F	3	VM	M	Mo
507	Commercial Spar No. 7	....	70	9	OK	5	E	3	OK	VM	Mo

The kauri numbers of these fifty-gallon varnishes naturally are high. The average kauri numbers for three modified synthetics sellings at 15 cents to 30 cents is 143—that for the much cheaper natural is 145. The gloss of the naturals is about the same as for the synthetics—these varnishes are not formulated for gloss—in special formulations it is well known that the naturals give better gloss than the synthetics. The natural resin varnishes have dried just as fast as those from synthetic resins. The China wood oil is the *primary* cause of rapid drying. The drier content of these varnishes is low. Four of the six natural resin varnishes are gas-proof—two of the modified synthetics are gas-proof. The natural resin varnishes gas-proof as well as the modified phenolics do. The hardness of the naturals is the same as that of the modified synthetics. The natural resin varnishes have withstood the action of boiling water for one hour perfectly as also have the synthetics. After four days in cold water each of the varnishes listed (except one commercial spar) has suffered a moderate loss of gloss. The natural resin varnishes passed the test as well as any of the synthetics.

One hour in boiling 5 per cent ivory soap has, as would be expected, softened nearly all of these fifty-gallon varnishes. The ones from bold black scraped and kauri are outstanding in their resistance and are definitely *superior* to any of the modified phenolics. The other naturals average as high as the modified phenolics.

To sum up the data from the entire series of these characteristic laboratory tests on the fifty-gallon varnishes, in every case the natural resins have equaled or exceeded the values of the modified phenolics which sell for much higher prices. This is a striking demonstration of the fact that natural resins give outstanding varnish-making values at remarkably low prices.

NATURAL RESINS

PHYSICAL PROPERTIES OF SINGLE RESIN 25-GALLON VARNISHES

No.	Resins	Per cent CWO	Kauri Number	Relative Gloss	Gas Proofness	Hours till tack free	Viscosity	Relative Hardness after 7days	Loss of gloss or softening after 1 hr. boiling water	1 hr. in5% Ivory Soap	4 days in water
2024	No. 1 Brown Kauri	90	100	7	F	2	C	4	OK	M	Mo
2020	No. 1 Brown Kauri	75	100	7	F	2½	B	4	OK	M	Mo
2022	Genuine Bold Pontianak	90	100	6	F	2	C	4	OK	M	Mo
2018	Genuine Bold Pontianak	75	100	8	F	2	D	3	OK	Mo	Mo
2016	Hard DarkAmber Congo	90	110	4	F	2	F	4	OK	M	Mo
2011	Hard Dark Amber Congo	75	100	4	F	2	E	4	OK	Mo	Mo
2038	Hard Light Amber Congo	90	90	7	F	2	C	4	OK	M	Mo
2013	Clean Ivory Congo	75	90	5	F	2	E	3	OK	M	Mo
2025	Bold Black E.I. Scraped	90	70	6	OK	2	F	3	OK	Mo	Mo
2028	Bold Black E.I. Scraped	75	60	7	F	2½	C	3	OK	M	Mo
2030	Batu Bold Scraped	90	70	7	F	2½	D	3	OK	Mo	Mo
2032	Batu Bold Scraped	75	70	8	F	2½	C	3	OK	Mo	Mo
2033	Pale Bold East India	90	50	7	F	2½	H	4	OK	M	Mo
2006	Pale Bold East India	100	80	6	F	3	G	3	OK	Mo	Mo
2010	Manila DBB Chips	75	80	7	F	2½	C	3	OK	Mo	Mo
2054	Boea Medium Dark	75	110	5	OK	2	B	4	OK	Mo	Mo
1013	Concentrated Phenolic No. 1	90	110	5	OK	3	E	3	OK	OK	OK
1012	Modified Phenolic No. 7	90	70	6	F	2½	B	3	VM	M	OK
1014	Modified Phenolic No. 5	90	70	6	F	3	C	3	OK	Mo	OK
1015	Modified Phenolic No. 8	90	50	8	F	3½	C	4	OK	OK	OK
502	Commercial SparNo. 2	....	60	4	OK	5	D	3	OK	VM	Mo
504	Commercial Floor No. 4	....	60	5	OK	5	E	4	OK	M	Mo
507	Commercial All Purpose No. 7	....	70	9	OK	5	E	3	OK	VM	Mo

NATURAL RESINS

The kauri numbers of these 25-gallon natural resin varnishes average much higher than those for the modified synthetics. The Boea Medium Dark and Hard Dark Amber Congo varnishes have kauri numbers as high as that of the varnish from the concentrated phenolic resin and they are more than double that of the varnish from the poorest modified phenolic resin. Ten of the sixteen natural resin varnishes have kauri numbers much higher than that of the best modified phenolic—only two of the poorest are as low as modified phenolic No. 8. Those of you who have seen the exhibits of panels in the Chicago and Washington Paint Industries Shows will remember that the *weather resistance shown by these panels was equally as favorable to the natural resins.*

The average gloss number of the sixteen natural resin varnishes is about 10% higher than that for all of the phenolics.

Two natural resin varnishes were gas proof, while not one of the varnishes from modified phenolics was gas proof. The drying rate of the natural resin varnishes exceeds that of the modified phenolics. The hardness of the naturals is greater than that of all the phenolics.

All of the varnishes passed the one hour in boiling water test except one modified phenolic which completely failed.

All but two varnishes were considerably softened by one hour in boiling soap solution. One concentrated and one modified phenolic varnish passed the test. The remainder of the phenolic varnishes and all of the natural resin varnishes were equally divided between *moderate* and *much* softening.

The natural resin varnishes suffered moderate loss of gloss but no rusting of the metal panels after four days in cold water, while the phenolics retained their gloss. In view of the superior weather resistance for the 25-gallon natural resin varnishes, this result is unexpected.

The purchased varnishes of type similar to these 25-gallon varnishes have shown low kauri numbers, greater gloss and gas proofness, slower drying and low resistance to boiling soap.

These tests of the 25-gallon varnishes again show the superior qualities of the natural resins—much higher kauri numbers than the modified phenolics, supported by weathering tests—as we shall see later—resistance to soap and cold water equal, or nearly equal, to the modified phenolics—greater gloss and hardness—*more rapid drying;* and every natural resin varnish passed the boiling water test, while one of three modified synthetics failed.

PHYSICAL PROPERTIES OF SINGLE RESIN 15-GALLON VARNISHES

No.	Resins	Per cent CWO	Kauri Number	Relative Gloss	Gas Proofness	Hours till tack free	Viscosity	Relative Hardness after 7 days	Loss of gloss or softening after 1 hr. boiling water	Loss of gloss or softening after 1 hr. in 5% Ivory Soap	Loss of gloss or softening after 4 days in water
2046	No. 1 Brown Kauri	90	30	7	F	3	C	5	OK	Mo	Mo
2045	Genuine Bold Pontianak	90	30	7	F	2½	B	5	OK	VM	OK
2050	Hard Dark Amber Congo	90	20	6	F	2	C	4	Mo	OK	Mo
2047	Bold Black Scaped	90	0	6	F	3	D	5	OK	VM	Mo
2048	Batu Bold Scraped	90	0	7	F	3	C	5	OK	VM	Mo
2049	Pale Bold East India	90	0	5	OK	2½	E	3	Mo	Mo	Mo
1017	Modified Phenolic No. 7	90	10	6	F	2½	B	4	OK	Mo	Mo
503	Commercial 4 Hr. Floor No. 3	....	0	6	OK	5	E	4	OK	VM	Mo
506	Commercial Quick Drying No. 6	....	0	9	OK	5	F	4	OK	VM	Mo
508	Commercial Floor No. 8	....	20	9	OK	5	D	4	OK	VM	OK

There were only a few varnishes in the 15-gallon group. The results of the laboratory tests on them are similar to those for the 25- and 50-gallon varnishes. The kauri numbers of the harder natural resin varnishes are 30, 30 and 20, as compared with 10 for the modified phenolic resin varnish. Even in these short oil varnishes where the ratio of China wood oil to resin is low the average drying rate of the natural resins equals that of the modified phenolic. The *gloss* and *hardness* of the natural resin varnishes are superior and their resistance to hot and cold water and boiling soap solution averages about the same as that of the synthetic resin varnish.

In following out this work the varnishes discussed have been made and their properties and values determined. It has been shown that, when compared with modified phenolic resins in high China wood oil content varnishes, they yield superior gloss and hardness and dry at least as rapidly as the modified phenolics do. Their resistance to hot and cold water and to boiling soap solution is excellent.

This demonstration of these qualities for natural resin varnishes containing high percentage of China wood oil strongly supports our claim that many values which have been widely credited to synthetic resins are actually due to China wood oil.

WEATHERING TESTS

In the following pages the weathering tests of a group of natural resin varnishes are described. For comparative purposes there is a discussion of control varnishes. In addition, the results of weathering of a group of varnishes made from natural resins, synthetic resins, and a mixture of these are described. The total number of varnishes subjected to weathering tests was greater than 400.

Photomicrographs and Illustrations

At various periods during the weathering, photomicrographs were taken of the partly weathered panels from a number of the varnishes. This permanent record permits a careful study of their condition and a comparison of their relative resistance to weathering. For photographing, the panels were carefully wiped with a soft damp cloth and placed face up on a table. A concentrated beam of light from a Bausch and Lomb illuminator was projected on the panel at a very oblique angle. A long bellows camera with a 10D Bausch and Lomb micro Tessar lens mounted vertically above the panel was focused upon it. The average distance from lens to ground glass was 33 c.m., giving a magnification of approximately 20 diameters, which is very satisfactory for this work.

Owing to the beam of light being so nearly parallel to the face of the panel, ridges or other elevations on the surface are strongly lighted and photograph white with deep shadows behind them. Cracks or other indentations show as dark areas and, if deep enough to go through the varnish film, are usually dead black. A deep crack from severe weather damage frequently is bordered by two parallel light-colored edges whose width indicates the extent to which weathering has gone under the film and rolled up thick lips on each side. With superficial checking or cracking the lips are absent or much less prominent, and the shallowness is indicated by the lighter color of the crack itself.

With wood panels, photomicrographs of a bare new panel, of panels on which the varnish is entirely undamaged, or of areas from which the varnish has been entirely weathered

away are all practically identical pictures showing merely the grain of the wood. Loss of gloss is shown by the extent to which the grain of the wood is obscured.

Weathering of the First Group Varnishes

These varnishes, brushed on 5"x10" steel, redwood and maple panels, were put on the test rack at Cincinnati on March 16, 1933, and weathered until the varnishes were completely destroyed.

Twenty-diameter photomicrographs were taken of representative areas on the redwood panels from many of the 25 and 50 gallon varnishes after twenty-four weeks of weathering.

No. 2006 is a 25-gallon Pale Bold East India varnish. After twenty-four weeks of weathering this varnish is only superficially damaged and is still giving complete protection to the panel. The very satisfactory character of its weathering is shown by its fine shallow checking and the absence of deep cracks which expose the panel. When this varnish is worn enough to require revarnishing a minimum amount of labor will be required to clean the surface.

No. 1012 is a 25-gallon varnish from modified phenolic resin No. 7, which is one of the best known on the market today. It also has been weathered for twenty-four weeks. In formulation, cooking methods and all other manipulation this resin has been given treatment as favorable to its requirements as that in No. 2007 and in all other varnishes of the group. The decidedly poorer weather resistance of this varnish as compared with No. 2006 is shown by the large area of bare wood from which all varnish has been removed by weathering. The blistered and deeply checked condition of the remainder of the varnish shows the extent to which weathering has gone under it. It is obvious that it has been a long time since the varnish has given any protection to the panel. A large amount of labor would be required to prepare this surface for revarnishing.

NATURAL RESINS

In addition to varnishes 2006 and 1012, similar photomicrographs of 25-gallon varnishes were made from:

Clean Ivory Congo.

Genuine Bold Pontianak.

Bold Scraped Batu.

Boea Medium Dark.

Modified Phenolic No. 5.

The results from these five varnishes are equally favorable to the natural resins, and the weather resistance of the poorest natural resin in the group is far superior to that of the best modified phenolic resin tested. Photomicrographs were also made of 50-gallon varnishes from:

Genuine Bold Pontianak.

Bold Black Scraped, East India.

Boea Medium Dark.

Modified Phenolic No. 5 and No. 6.

In this group the weather resistance of the poorest natural resin varnish was definitely better than that of the varnish from either of these well-known modified phenolic resins.

With both groups the natural resin varnishes have weathered by such fine checking that the surface will require little or no labor to prepare for revarnishing. On the contrary, each of the modified phenolic resin varnishes on weathering has left a surface which will require laborious preparation for revarnishing.

These natural resin varnishes all dry as rapidly and are as gas-proof as those from the modified phenolics, and most of them have superior gloss and hardness. Their average resistance to hot and cold water and to boiling 5% soap solution is equal or superior.

Formulation: Varnishes of the Second Group

All of the 300 varnishes of this group have been based on a single type formula and the individual varnishes vary only in the resin used and in gallonage. As shown in the accompanying charts, the main groups are 15, 25 and 50 gallon varnishes from seven natural resins and from three concentrated phenolic resins. These are used in control varnishes each containing only one resin and also in mixtures containing 50% or 75% of natural resin blended with a single concentrated phenolic resin. These concentrated phenolics were of the makes most widely advertised and used in the Spring of 1934. In addition to the above, control varnishes were also made from three additional concentrated and eight modified phenolic resins, and a group of well-known spar, all purpose and floor varnishes were purchased and tested.

Another main group of 25-gallon varnishes was made from mixtures of natural and modified phenolic resins with control varnishes similar to those of the first group. These four groups of varnishes are described in the charts printed here.

The typical formula for a 25-gallon varnish is:

400 Resin.
680 China wood oil.
120 Four-hour linseed oil.
960 Varnolene.
240 Hi Flash naptha.

The hi flash naptha was used in all of the varnishes because some of the concentrated phenolics required it.

Cooking

In cooking these varnishes the aim has again been to make the entire group as comparable as possible and still allow for the individual requirements of the various resins used. The natural resins were run and then the China wood oil, heated to 400°F., was added. The varnish was bodied at 450°F., then checked with the bodied linseed oil and the thinners added. With the mixed resin varnishes the concen-

trated phenolic resin was added just after the China wood oil and the two resins and oil were cooked together to the proper body, after which the check oil and thinners were added. The control varnishes from concentrated and modified and phenolic resins were cooked as recommended by their manufacturers. These cooks were in many cases similar to the above.

After standing for a week or more, the varnishes were contrifuged and soluble type driers added. These were calculated as metals and based on the drying oil content of the varnish. The quantity used is shown on the charts.

Testing

Five-by-ten-inch steel, redwood and maple panels for weathering and 3"x5" steel and tin panels for laboratory tests were prepared from these varnishes as for the earlier group. A similar series of laboratory tests was run on the entire group of varnishes. These tests show results similar to those of the first group.

Weathering

The panels were put on the test rack at Cincinnati on March 16, 1934. They were inspected every four weeks and records kept in the usual manner. After forty weeks they were removed from the rack and stored. Twenty-diameter photomicrographs were taken of the maple panels from a number of the 15-gallon varnishes after twenty-four weeks, of 25-gallon varnishes after thirty-two weeks, of 50-gallon varnishes after thirty-eight weeks and of many of them again after the panels were removed from the rack. A number of the panels were also photographed at this time. All had been weathered for forty weeks.

NATURAL RESINS

15-Gallon Varnishes

No. 2080	No. 1 Brown Kauri.
2081	Hard Dark Amber Congo (No. 11).
3121	(75% Hard Dark Amber Congo (No. 11).
	(25% Conc. Phenolic Resin No. 1.
1073	Concentrated Phenolic Resin No. 3.
1074	Modified Phenolic Resin No. 11.
1077	Modified Phenolic Resin No. 12.
518	Commercial Floor Varnish No. 7.

25-Gallon Varnishes

No. 2057	No. 1 Brown Kauri.
2059	Boea Medium Dark.
2062	Hard Dark Amber Congo (No. 11).
1043	Modified Phenolic No. 11.
1091	*Modified Phenolic No. 5.
1092	*Modified Phenolic No. 8.
526	Commercial All Purpose No. 15.

*These were 31¼-gallon varnishes.

50-Gallon Varnishes

No. 2066	Bold Black Scraped.
2069	Boea Medium Dark.
3057	(75% No. 1 Brown Kauri.
	(25% Conc. Phenolic No. 1.
1050	Modified Phenolic No. 10.
1056	Modified Phenolic No. 4.
1058	Modified Phenolic No. 6.
519	Commercial Spar No. 8.

The photographs of weathered panels from 15-gallon varnishes show the excellent qualities of Congo resins in an outstanding way. After forty weeks of weathering this 15-gallon Congo Varnish No. 2081 is still giving complete protection to the panel. The film is entirely free from cracking, peeling or other severe breakdown, except at the single point where the panel has cracked from moisture entering at its lower end. The clear picture of its wood grain is in marked contrast to the damaged and scarred appearance of every one of the modified phenolic resins regardless of price.

NATURAL RESINS

15-Gallon Varnishes From Mixtures of Natural and Synthetic Resins

85% C. W. O.—15% L. O.—50% Non-volatile soluble type drier—0.4% Lead, 0.03% Manganese and 0.0088% Cobalt

One varnish was made corresponding to the composition indicated by each "X" in the chart.		Concentrated Phenolic Resins									Ester Gum	
		#1			#2			#3				
		25%	75%	100%	25%	75%	100%	25%	75%	100%	25%	100%
				X			X			X		X
Genuine Bold Pontianak	75%		X			X			X			X	
Genuine Bold Pontianak	100%	X										
Manila DBB Chips	75%		X			X			X			X	
Manila DBB Chips	100%	X										
Boea Medium Dark	75%		X			X			X			X	
Boea Medium Dark	100%	X										
No. 1 Brown Kauri	75%		X			X			X			X	
No. 1 Brown Kauri	100%	X										
Bold Black Scraped E. I.	75%		X			X			X			X	
Bold Black Scraped E. I.	100%	X										
Batu Bold Scraped	75%		X			X			X			X	
Batu Bold Scraped	100%	X										
Hard Dark Amber Congo (No. 11)	75%		X			X			X			X	
Hard Dark Amber Congo "	100%	X										
Ester Gum	25%			X			X			X			
Ester Gum	75%		X			X			X				

Single resin control varnishes were also made from two concentrated and eight modified phenolic resins.

NATURAL RESINS

25-Gallon Varnishes From Mixtures of Natural and Synthetic Resins

85% C. W. O.—15% L. O.—50% Non-volatile soluble type drier—0.4% Lead, 0.03% Manganese and 0.0088% Cobalt

One varnish was made corresponding to the composition indicated by each "X" in the chart.		Concentrated Phenolic Resins												Ester Gum		
		#1				#2				#3						
		25	50	75	100	25	50	75	100	25	50	75	100	25	50	100
					X				X				X			X
Genuine Bold Pontianak	50%		X				X				X				X	
" " "	75%	X				X				X				X		
" " "	100%	X														
Manila DBB Chips	50%		X				X				X				X	
" " "	75%		X				X				X			X		
" " "	100%	X														
Boea Medium Dark	50%		X				X				X				X	
" " "	75%	X				X				X				X		
" " "	100%	X														
No. 1 Brown Kauri	50%		X				X				X				X	
" " "	75%	X				X				X				X		
" " "	100%	X														
Bold Black Scraped E. I.	50%		X				X				X				X	
" " " "	75%	X				X				X				X		
" " " "	100%	X														
Batu Bold Scraped	50%		X				X				X				X	
" " "	75%	X				X				X				X		
" " "	100%	X														
Hard Dark Amber Congo(No.11)	50%		X				X				X				X	
" " " " "	75%	X				X				X				X		
" " " " "	100%	X														
Ester Gum	25%			X				X				X				
" "	50%		X				X				X					
" "	75%	X				X				X						

Single resin control varnishes were also made from three concentrated and eight modified phenolic resins.

25-Gallon Varnishes From Mixtures of Natural and Synthetic Resins

85% C. W. O.—15% L. O.—50% Non-volatile soluble type drier—0.4% Lead, 0.03% Manganese and 0.0088% Cobalt

One varnish was made corresponding to the composition indicated by each "X" in the chart.		Modified Phenolic Resins											
		#7				#5				#9			
		50%	75%	100%		50%	75%	100%		50%	75%	100%	
				X				X				X	
Hard Dark Amber Congo(No.11)	25%		X				X				X		
" " " " "	50%	X				X				X			
" " " " "	100%	X											
Sorts Congo (No. 12)	25%		X				X				X		
" " "	50%	X				X				X			
" " "	100%	X											
No. 1 Brown Kauri	25%		X				X				X		
" " "	50%	X				X				X			
" " "	100%	X											
Pale Bold East India	25%		X				X				X		
" " " "	50%	X				X				X			
" " " "	100%	X											

NATURAL RESINS

50-Gallon Varnishes From Mixtures of Natural and Synthetic Resins

85% C. W. O.—15% L. O.—50% Non-volatile soluble type drier—0.4% Lead, 0.03% Manganese and 0.0088% Cobalt

One varnish was made corresponding to the composition indicated by each "X" in the chart.		Concentrated Phenolic Resins												Ester Gum		
		#1				#2				#3						
		25	50	75	100	25	50	75	100	25	50	75	100	25	50	100
					X				X				X			X
Genuine Bold Pontianak	50%		X				X				X				X	
" " "	75%	X				X				X				X		
" " "	100%	X														
Manila DBB Chips	50%		X				X				X				X	
" " "	75%	X				X				X				X		
" " "	100%	X														
Boea Medium Dark	50%		X				X				X				X	
" " "	75%	X				X				X				X		
" " "	100%	X														
No. 1 Brown Kauri	50%		X				X				X				X	
" " "	75%	X				X				X				X		
" " "	100%	X														
Bold Black Scraped E. I.	50%		X				X				X				X	
" " " "	75%	X				X				X				X		
" " " "	100%	X														
Batu Bold Scraped	50%		X				X				X				X	
" " "	75%	X				X				X				X		
" " "	100%	X														
Hard Dark Amber Congo(No.11)	50%		X				X				X				X	
" " " " "	75%	X				X				X				X		
" " " " "	100%	X														
Ester Gum	25%			X				X				X				
" "	50%		X				X				X					
" "	75%	X				X				X						

Single resin control varnishes were also made from three concentrated and eight modified phenolic resins.

The photomicrograph of No. 2081 shows the very fine and superficial checking by which this varnish is weathering. Comparison of it with No. 1077 or any of the other six photomicrographs of modified phenolic resins of various gallonages, or after exposures of from twenty-four to forty weeks, shows the advantageous way in which it is weathering and its actual great durability in most of these cases. No. 1080 and No. 1012 are 15 and 25 gallon varnishes from well-known modified phenolic resins No. 8 and No. 7 after only twenty-four weeks' exposure. Both of these have failed completely. No. 1056 is a 50-gallon varnish from a still higher priced modified phenolic resin. After thirty-eight weeks of weathering it is deeply cracked and has completely failed in many places. These results are evidence that the longer gallonage resulting in the loss in weight when natural resins are run does not in any way explain the greater weather resistance of natural resin varnishes, as compared with equivalent varnishes from modified phenolic resins.

Panels from 25-gallon varnishes compare the weather resistance of a hard Manila (Boea Medium Dark) and a modified phenolic resin. Varnish No. 1091 and two others were made in 31¼ gallon length to be the equivalent of a 25-gallon natural resin varnish, in which 20% of the weight of the resin is lost during running. The complete protection which the Boea Varnish No. 2059 is still giving is evident from its clean surface and the perfect picture of the wood grain which shows through it. The cracking and extensive failure of Varnish No. 1091 has been characteristic of each of the three well-known modified phenolic resins tested. As compared with the three modified phenolics, the natural resins have shown greatly superior durability and also a freedom from that type of failure which makes revarnishing difficult. The comparison between the 25-gallon varnishes from No. 2006 Pale Bold East India and No. 1012 Modified Phenolic No. 7 after twenty-four weeks of weathering shows the complete failure of the phenolic resin varnish as contrasted with the fine grained superficial checking of the East India varnish.

The results from these 50-gallon varnishes are similar to those from the 15 and 25 gallon groups. The exceptional durability of this Bold Black Scraped varnish is especially notable in so low priced a resin. Its excellent gloss retention and the very slight damage it has suffered in forty weeks as compared with that suffered by No. 1050 and No. 1056, which are 50-gallon varnishes from medium and high-priced modified phenolic resins, strikingly demonstrate the high quality of this natural resin. Comparison of photomicrographs No. 2066 and No. 2063 with No. 1050 and No. 1056 yields further evidence of the superior weather resistance of Bold Black Scraped and Genuine Pontianak resins. Similar properties were shown for Boea Medium Dark.

Results from laboratory and weathering tests on comparatively high China wood oil content 15, 25 and 50 gallon varnishes from natural and modified phenolic resins have demonstrated many valuable properties that have not been generally credited to natural resin varnishes.

The results of the laboratory tests demonstrate that China wood oil has given rapid drying to natural resin varnishes and resistance to these tests which equals or exceeds that of modified phenolic resin varnishes. In this way they justify the belief that many values which have come to be generally attributed primarily to modified phenolic resins have been to a large extent given to them by the use of large amounts of China wood oil in their varnishes.

The weather tests have shown that in each gallonage several of the natural resin varnishes have had greatly superior weather resistance than comparative varnishes from well-known modified phenolic resins. That this is true regardless of the greater gallonage due to loss in weight of the natural resin on running is shown by comparing 25-gallon natural resin varnishes with 31¼-gallon varnishes from modified phenolic resins. It is also shown by the fact that the 15-gallon Congo varnish was in much better condition after forty weeks' weathering than either of the three 31¼-gallon modified phenolic resin varnishes. Congo resin has shown outstanding weather resistance in both 15 and 25 gallon varnishes.

HEAT TREATING NATURAL RESINS TO MAKE THEM OIL SOLUBLE

As natural resins come to the varnish maker, many of them must be given a thermal treatment called "running," "melting," or "cracking" to make them oil soluble. This is done by heating the resin in a kettle until a homogeneous thin liquid, free from lumps or gummy masses is obtained. During this process, volatile oils are distilled off in variable quantities depending upon how the procedure is carried out. If the cover is left on the kettle, a larger amount of the high boiling portions of the oil are retained and the resin becomes oil soluble with minimum loss in weight. The resulting varnishes are, however, not as hard as those prepared in an open kettle with greater loss of volatile material. The loss in weight of resin during running varies from about 10% to about 35%, depending on the resin and on the procedure used. Under average conditions the loss is 15% to 20%.

Though the intensity and duration of the heating are varied by the varnish technician for making varnishes of special types, it is not difficult to determine the point at which the resin has become oil soluble. At this point all lumps, spongy or gummy masses, and all or nearly all of the foam will have disappeared. The resin will have melted to a thin uniform liquid which will flow or drip from the stirring rod or paddle like hot oil. The varnish is then completed by adding the oils and other resins to be used. Care should be taken to avoid too sudden chilling and solidifying of the run resin.

The following are examples of the methods of running the three most frequently used types of natural resins. These methods will assure obtaining oil soluble resins. In commercial practice the procedures and temperatures used vary widely.

NATURAL RESINS

CONGO RESINS

Heat the resin to 600° F. during about one hour. Hold at 600° F. until all the resin is plastic all the hard lumps have been disintegrated and the foam has begun to subside (approximately one hour). Stir occasionally to avoid local overheating. Raise temperature to 650° F. and hold until all of the resin is liquid and will drip from the paddle like hot oil (approximately 15 minutes).

HARD MANILA RESINS

Heat the resins to 625° F. during about an hour with occasional stirring. Let cool to 500° F. to 550° F. Heat to 600° F. and hold until all of the resin is liquid and will drip from the paddle like hot oil (about an hour).

EAST INDIA RESINS

Heat the resin to 600° F. during about an hour with occasional stirring, and hold until all of the resin is liquid and will drip from the paddle like hot oil (about an hour).

VARNISH FORMULATIONS

No. 468—8-gallon Hard Dark Amber Congo (No. 11)

All China Wood Oil

	Pounds	
100 pounds	1000	Hard Dark Amber Congo (No. 11)
8 gals.	620	China Wood Oil
30 gals.	1950	Varnolene

0.4% lead, 0.03% manganese, 0.01% cobalt calculated as metals and based on the drying oil.

Heated the resin in kettle without cover to 650° F. during one hour, held for 1¾ hours, off fire, slowly added China wood oil pre-heated to 400° F. Heated from 465° F. to 560° F., held for body, cooled to 420° F., added thinner. The soluble type driers were added after centrifuging.

Loss in weight of Congo on running—34%.

VARNISH FORMULATIONS

No. 469—15-gallon Hard Dark Amber Congo (No. 11)

80% China Wood Oil

	Pounds	
100 pounds	1000	Hard Dark Amber Congo (No. 11)
12 gals.	930	China Wood Oil
3 gals.	240	No. 00 Pale Linseed
34 gals.	2210	Varnolene
1¾ gals.	17.2	Cryst. Lead Acetate

0.08% lead cooked in the varnish, 0.03% manganese and 0.01% cobalt added after centrifuging.

Heated the resin in kettle without cover to 650° F. during one hour, held one hour, added China wood oil pre-heated to 400° F., heated from 465° F., to 560° F., added bodied linseed oil and then the lead acetate. Held 518° F. for ½ hour, Cooled to 480° F., added thinner.

Loss in weight of Congo on running—33%.

VARNISH FORMULATIONS

No. 470—25-gallon Hard Dark Amber Congo (No. 11)

80% China Wood Oil

	Pounds	
100 pounds	1000	Hard Dark Amber Congo (No. 11)
20 gals.	1550	China Wood Oil
5 gals.	400	No. 00 Pale Bodied Linseed
46 gals.	2990	Varnolene

0.4% lead, 0.03% manganese, and 0.01% cobalt added after centrifuging.

Heated the resin in kettle without cover to 650° F. during one hour. Held one hour, removed cover, added China wood oil pre-heated to 400° F., heated from 465° F. to 560° F. Added the linseed oil, held to body at 518° F. to 450° F., added thinner.

Loss in weight on running the Congo—20%.

VARNISH FORMULATIONS

No. 471—8-gallon Boea Medium Dark

All China Wood Oil

	Pounds	
100 pounds	1000	Boea Medium Dark
8 gals.	620	China Wood Oil
30 gals.	1950	Varnolene

0.4% lead, 0.03% manganese, and 0.01% cobalt added after centrifuging.

Heated the resin in kettle with cover to 625° F. during one hour, off fire for 15 minutes cooling to 518° F., heated to 610° F. and held for one hour, removed cover, off fire and added China wood oil pre-heated to 400° F., heated from 482° F. to 560° F. and held to body at 560° F. to 400° F., added thinner.

Loss in weight of the Boea on running—20%.

VARNISH FORMULATIONS

No. 472—15-gallon Boea Medium Dark

80% China Wood Oil

	Pounds	
100 pounds	1000	Boea Medium Dark
12 gals.	930	China Wood Oil
3 gals.	240	No. 00 Pale Bodied Linseed
34 gals.	2210	Varnolene
1¾ gals.	17.2	Cryst. Lead Acetate

0.8% lead cooked in the varnish, 0.03% manganese and 0.01% cobalt added after centrifuging.

Heated the resin in kettle with cover to 625° F. during one hour, held for one hour, removed cover, slowly added China wood oil pre-heated to 400° F., heated from 482° F. to 560° F., added linseed oil, held to body at 518° F. Cooled and added thinners.

Loss in weight of the Boea on running—20%.

VARNISH FORMULATIONS

No. 473—25-gallon Boea Medium Dark

80% China Wood Oil

	Pounds	
100 pounds	1000	Boea Medium Dark
20 gals.	1550	China Wood Oil
5 gals.	400	No. 00 Pale Bodied Linseed
46 gals.	2990	Varnolene

0.4% lead, 0.03% manganese, and 0.01% cobalt added after centrifuging.

Heated the resin in kettle with cover to 625° F. during one hour, held for one hour, removed cover, slowly added China wood oil pre-heated to 400° F., heated from 465° F. to 560° F. Added the linseed oil, held to body at 518° F. to 450° F., added thinners.

Loss in weight of the Boea on running—20%.

VARNISH FORMULATIONS

No. 474—8-gallon Bold Black Scraped E. I.

All China Wood Oil

	Pounds	
100 pounds	1000	Bold Black Scraped E. I.
8 gals.	620	China Wood Oil
30 gals.	1950	Varnolene

0.4% lead, 0.03% manganese, and 0.01% cobalt added after centrifuging.

Heated the resin in kettle with cover to 610° F. during one hour, off fire for 10 minutes cooling to 482° F. Heated to 625° F. for one hour, removed cover, poured in China wood oil pre-heated to 400° F., heated from 500° F. to 560° F., held to body at 560° F. 450° F., added thinner.

Loss in weight of Bold Black Scraped on running—15%.

VARNISH FORMULATIONS

No 475—15-gallon Bold Black Scraped E. I.

80% China Wood Oil

		Pounds	
100	pounds	1000	Bold Black Scraped E. I.
12	gals.	930	China Wood Oil
3	gals.	240	No. 00 Pale Bodied Linseed
34	gals.	2210	Varnolene
1¾	gals.	17.2	Cryst. Lead Acetate

0.08% lead cooked in the varnish, 0.03% manganese and 0.01% cobalt added after centrifuging.

Heated the resin in kettle with cover to 610° F. during one hour, off fire to 500° F., heated to 625° F. and held for one hour, removed cover, off fire and added China wood oil pre-heated to 400° F., heated from 482° F. to 560° F., added linseed oil, held to body at 518° F., cooled and added thinner.

Loss in weight of Bold Black Scraped on running—15%.

VARNISH FORMULATIONS

No. 476—25-gallon Bold Black Scraped E. I.

80% China Wood Oil

	Pounds	
100 pounds	1000	Bold Black Scraped E. I.
20 gals.	1550	China Wood Oil
5 gals.	400	No. 00 Pale Bodied Linseed
46 gals.	2990	Varnolene

0.4% lead, 0.03% manganese, and 0.01% cobalt added after centrifuging.

Heated the resin in kettle with cover to 610° F. during one hour, off fire to 482° F., heated 625° F. and held for one hour, off fire, removed cover and added the China wood oil pre-heated to 400° F., heated from 500° F. to 560° F. and added the linseed oil, held to body at 518° F. to 450° F., added thinner.

Loss in weight of Bold Black Scraped on running—15%.

DATA ON VARNISHES

Number	Natural Resin	Length, Gallons	Viscosity	Color	Gas Test	Dust Free Hours	Tack Free Hours	Hardness A.D. 24 Hours	Hardness A.D. 72 Hours	Relative Gloss	Color of Varnish Film	Gloss	Hardness	1 Hour in 5% Caustic	1 Hour in Boiling 5% Ivory Soap Solution
												In distilled water for 4 days			
468	Hard Dark Amber Congo No. 11	8	F	18	OK	1	3	2	5	5	LYB	OK	OK	VM	VM
469	" " " "	15	E	17	OK	1	3	1	4	5	LYB	Sl	Sl	VM	VM
470	" " " "	25	G	15	F	1	3	1	2	8	L	Sl	Sl	VM	VM
471	Boea Medium Dark	8	G	16	OK	1	3	1	5	8	LYB	OK	OK	VM	VM
472	" "	15	E	17	OK	1	3	1	4	6	LYB	Sl	Sl	VM	VM
473	" "	25	G	15	F	1	3	1	2	9	L	Sl	Sl	VM	VM
474	Bold Black Scraped E. I.	8	E	18+	OK	1	4	1	4	8	YB	OK	OK	Mo	Mo
475	" " " "	15	E	18+	OK	1	4	1	3	9	YB	Sl	Sl	VM	VM
476	" " " "	25	G	18+	F	1	4	1	2	6	LYB	Sl	Sl	VM	VM

Viscosity and Color by Gardner-Holdt Standards.
Gas Test— F — panels that had dried 2/5, 3/5 and 4/5 of the time required to set to touch failed the gas test.
Larger numbers indicate greater hardness or gloss.
Color of varnish on white enameled panels: L—light, YB—yellowish brown.
Four days in distilled water—Gloss or Hardness—Sl—slight loss.
In 5% Caustic or Boiling Ivory Soap—VM—very much softening; Mo—moderate softening.

VARNISHES FROM MIXTURES OF NATURAL AND PHENOLIC RESINS

Two groups of these have been made.

1. Blends of natural resins with concentrated phenolic resins.
2. Blends of natural resins with modified phenolic resins.

Blends with Concentrated Phenolic Resins

Fifteen, 25 and 50 gallon varnishes have been made from blends of natural resins with 25% and with 50% of several well known concentrated phenolic resins. Similar blends of ester gum with concentrated phenolic resins were made for comparison. These natural resin varnishes are gas proof, dry very rapidly and have excellent gloss, hardness, adhesion, and weather resistance.

Formulation and Cooking

The oils in both groups of varnishes are 85% China wood oil and 15% bodied linseed. A typical 75% natural resin —25% concentrated phenolic 15 gallon varnish is No. 327.

Pounds	
450	Hard Dark Amber Congo (No. 11)
150	Concentrated Phenolic No. 2
594	China Wood Oil
108	No. 0 Bodied Linseed
654	Varnolene
648	Toluol

The Congo was run in the usual way, after which the China wood oil, pre-heated to 400° F., and then the concentrated phenolic resin were added. The cook was held at 450° F. to the desired body, the bodied linseed was added, and the varnish thinned and centrifuged. Later soluble type driers equal to 0.4% lead, 0.03% manganese, and 0.0088% cobalt calculated on the drying oil were added. This entire group of varnishes, except for the resins used, were of identical formulation. The concentrated phenolic resins used were ones which cook well at 450° F. The comparisons made are between varnishes of this group, all of which have received identical treatment.

Blends with Modified Phenolic Resins

This group of 25 gallon varnishes was made from natural resin blended wtih 50% and 75% of well known modified phenolic resins.

Formulation and Cooking

A typical formula for the 25 gallon 50:50 blends of natural and modified phenolic resins is No. 396:

Pounds	
200	Hard Dark Amber Congo (No. 11)
200	Modified Phenolic Resin No. 9
680	China Wood Oil
120	No. 0 Bodied Linseed Oil
1200	Varnolene

The Congo was run in the usual way after which the preheated China wood oil and then the modified phenolic resin were added and the batch heated to 560° F. The bodied linseed was added and the varnish bodied on the down heat and thinned. After centrifuging, driers were added as for the previous cook.

The modified phenolic resins used were ones which are usually cooked at 560°. Here again identical formulation and treatment make comparisons between the several varnishes of the group valid.

The control varnishes, containing modified phenolic resins only, were cooked in a similar manner at 560° F.

WEATHERING OF MIXED RESIN VARNISHES

Tests in Cincinnati and Florida

As duplicate weathering tests were made in the two places, direct comparisons are possible. The eight-month Florida exposures were from July to April, inclusive, omitting two winter months, during which the panels were not exposed. The thirteen-month Cincinnati exposures included an entire year's cycle plus an extra summer month. Comparison of the monthly reports from these and other test runs have shown that during severe summer conditions, weathering is as rapid in Cincinnati as in Florida, but that this is more than made up for by the more severe weathering in Florida during the remainder of the year. In these tests the eight-month Florida weathering caused somewhat more destruction than the thirteen-month Cincinnati weathering.

Weathered Varnishes from Mixtures of Natural and Concentrated Phenolic Resins

The varnishes of this group were made to demonstrate the relative values of natural resin and of ester gum as modifying and diluting agents for concentrated phenolic resins. In them, ester gum shows its characteristic failure through forming wide deep cracks with weathering undermining the varnish at the edges. This tendency has been greater than even 50% of concentrated phenolic resin could overcome, and bare panel is exposed in cracks while the varnish elsewhere still has considerable gloss and thickness.

On the other hand, natural resins have confirmed previous results by weathering uniformly over the whole surface in a manner similar to chalking.

Fifteen Gallon Varnishes

Varnishes were made containing 75% each of several varieties of natural resins or of ester gum blended with 25% of several well known concentrated phenolic resins. Maple panels with three coats of varnish were weathered for nine months in Cincinnati.

The superior weather resistance of varnishes containing Hard Dark Amber Congo, Boea Medium Dark, and Batu as compared with ester gum was illustrated by examination of the panels and of 30 diameter photomicrographs and pictures of whole panels.

The comparatively slight damage suffered by varnishes from the Congo and Batu blends with concentrated phenolic resin No. 3 and its uniform character are clearly shown. The fine superficial checking nowhere exposes the panel and is in strong contrast with the irregular checking cracking, and exposure of bare wood shown by the ester gum blend. The whole panel pictures (No. 327 and No. 328, 75% Congo—25% concentrated phenolic No. 2) from the natural resin blends show an unobstructed view of the grain and color tones of the maple panel, while the panels (No. 348 and No. 350) from ester gum with two concentrated phenolic resins both show such extensive damage that bare panel is exposed in many places and protection is entirely destroyed.

Fifty Gallon Varnishes

A group of varnishes similar to those in the fifteen gallon series was made from five natural resins and ester gum, blended with well known concentrated phenolic resins. Photomicrographs and panel pictures of these after nine months Cincinnati weathering were shown at Production Club meetings.

The photomicrographs from 75% blends of Batu and Boea show a sharp picture of the grain of the wood through the clear varnish. Practically no checking or chalking has occurred.

In contrast with this, varnish No. 280 containing 75% of ester gum has cracked wide open over the entire surface. Even in ester gum varnish No. 281, where the quantity of the costly phenolic resin has been doubled, there is extensive damage and areas of bare panel occur.

The natural resin varnishes No. 254 and No. 270 have given remarkably better weather resistance than either No. 280 at about the same price or No. 281 at a much higher price. These economies, in addition to the better adhesion, gloss, etc., obtained from natural resins, show their striking superiority over ester gum for blending with concentrated phenolic resins.

Weathered Varnishes from Mixtures of Natural and Modified Phenolic Resins

These 25 gallon varnishes contain 50% and 25% blends of various natural resins with several well known modified phenolic resins. Single resin control varnishes containing well known modified phenolic resins only were also made and tested.

The results discussed below are from maple panels with three coats of varnish weathered for thirteen months in Cincinnati.

Photomicrographs and whole panel pictures were made from many of the weathered panels. Those from blends of Hard Dark Amber Congo, No. 5 Sorts Congo, and East India with several modified phenolic resins and from the modified phenolic resins alone, were carefully examined.

These results confirm and extend those of last year and show conclusively that the addition of natural resins to modified phenolic resin varnishes greatly improves their weather resistance. In varnish No. 389 the ester gum in the modified phenolic resin has caused its characteristic failure by severe cracking, exposing bare panel. The addition of 25% of Congo in No. 405 has considerably improved the weather resistance of the varnish. Varnish No. 404 containing 50% of Congo has shown only superficial checking after thirteen months weathering. This outstanding improvement through the use of natural resins in such varnishes is shown in both the photomicrographs and whole panel pictures. The more satisfactory type of weathering caused by the natural resins is shown by the freedom from premature cracks and the gradual and uniform chalking or wearing out of the varnishes over the entire area of the panel.

METHODS OF TESTING NATURAL RESINS

On the following pages are detailed a number of testing methods for natural resins. In reference to the entire general subject, reference should be made to Gardner "Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors," either the 1933 or the 1935 edition. For specific references where the methods in this booklet differ from Gardner or are modifications, the following are to be noted:

Melting point—Gardner 1933, page 719; 1935, page 837

Specific gravity—Gardner 1933, page 743; 1935, page 875

Direct acid number—Gardner 1933, page 723; 1935, page 846

Color—Gardner 1933, page 161; 1935, page 191

Viscosity—Gardner 1933, page 494; 1935, page 562

Hardness—Gardner 1933, page 206; 1935, page 296

NATURAL RESINS

A number of testing methods have been developed in the laboratories of the American Gum Importers Association in the course of research work on natural resins. These are detailed below.

PHYSICAL CHARACTERISTICS

1. **Insoluble content.**—One gram of the sample is dissolved in an appropriate solvent (generally toluol for damar resins, ethyl alcohol for Manila resins). The solution is warmed and filtered on a dried and weighed asbestos Gooch filter. After washing with several portions of hot solvent the Gooch is dried to constant weight and the per cent insoluble calculated from the gain in weight of the Gooch. The results from this method are not entirely satisfactory, as some resins, especially the Manilas, contain small percentages of resene-like material for which no solvent can be found, but no more accurate method has as yet been devised.

2. **Deposition test for insolubles.**—Transfer 10 grams of a representative sample to a 50 cc. graduated cylinder bottle, add 40 cc. of U.S.P. 95 per cent ethyl alcohol, insert the cork firmly, and shake until all of the alcohol-soluble material is in solution. The test is to be run in duplicate. Then set aside for 24 hours to permit the insoluble matter to settle. Allow the solution or "cutting" to stand overnight. Upon inspection the next morning, if the deposition in the bottom of the cylinder is found not to be level, place the bottle in such a position that by inclining it in the proper direction momentarily, or in the event that this is not sufficient, by tapping the bottom of the bottle against the bench judiciously, the proper level is established. Then allow the cylinder to rest until the 24 hour period has elapsed, whereupon the deposition is carefully read off in cc. or fraction thereof, and a report of this reading made. The average of two readings is to determine the amount of insoluble matter.

3. **Moisture content,** first method.—2-3 grams of the finely ground sample is spread out in an inverted can lid about 5 cm. in diameter and left 3 hours in an oven at 105° C. The loss in weight is assumed to be moisture.

3-a. **Moisture content,** second method.—The apparatus required is a constant temperature electric oven. The procedure calls for 5 grams of a powdered sample in a flat-bottomed dish about 4 inches in diameter. The dish is placed in a well ventilated electric oven for at least 6 hours at 60° C. ± 2° C. The sample is cooled in a desiccator and weighed. Heating is continued to constant weight and the weight loss calculated as percentage moisture.

4. **Melting point.**—0.2 gram of the sample is gently sintered to the bottom of a wide form porcelain crucible of about 17 cc. capacity. 100 grams of mercury, previously heated to about 30° below the probable melting point of the resin, is poured in on top of the sample, and a thermometer is immersed in the mercury. The crucible is heated slowly (2°-4° per minute). The temperature at which the first bit of resin appears above the surface of the mercury is reported as the melting point. The original statement of this method (Journal of the Oil and Colour Chemists' Association, vol. 13, p. 287 (1930)) prescribes 25 grams of mercury, but the larger amount has been found to give the same values and to be easier to handle.

5. **Softening point.**—Some of the ground sample is placed in a capillary melting point tube and heated in a liquid bath. The temperature at which the sharp edges of the resin fragments appear to start becoming round is reported as the softening point. This is a rather indefinite value and difficult for two operators to agree upon. It is of less significance than the melting point value.

6. **Specific gravity.**—A series of salt solutions of specific gravity 1.020, 1.030, 1.040, etc., as checked with a Westphal balance, is made up. A piece of the resin sample is thoroughly wet with water, then dropped into each solution. The specific gravity of the resin is reported as that of the least dense salt solution in which it will float.

CHEMICAL CHARACTERISTICS

7. **Direct acid number.**—1 gram of the sample is dissolved in a mixture of 50 cc. toluol and 50 cc. ethyl alcohol in a 500 cc.

Erlenmeyer flask. (Note: Damar samples are dissolved in the toluol first, then the alcohol is added and the mixture allowed to stand 2-4 hours before titrating.) After standing a few minutes the solution, cloudy in the case of damar resins, is titrated with a 0.1N solution of alcoholic potassium hydroxide, using phenolphthalein as an indicator. Blank determinations are run at the same time. The acid value is reported as the number of milligrams of potassium hydroxide required per gram of resin.

8. **Indirect acid number.**—To the mixture obtained in the determination of the direct acid number is added 5-10 cc. excess 0.1N potassium hydroxide. The flask is stoppered and allowed to stand at room temperature over night. The mixture is then titrated back with aqueous 0.1N sulphuric acid. The indirect acid value, like the direct, is calculated as milligrams potassium hydroxide per gram of resin. Blank determinations are run each time.

9. **Iodine number.**—The Hübl method is employed. 25 grams of iodine is dissolved in 500 cc. of 95 per cent alcohol. The "iodine solution" is prepared by mixing these two solutions and allowing it to stand 12-24 hours. 0.2 gram of the sample is dissolved in 10 cc. of pure carbon tetrachloride in a 500 cc. flask. 25 cc. of the iodine solution is run in from a pipette and the flask is stoppered and allowed to stand in the dark over night. Then 15 cc. of a 10 per cent aqueous solution of potassium iodide is added, the liquid is well shaken and diluted with 250 cc. of water. The excess of free iodine is titrated with a standard solution of sodium thiosulphate, adding a few drops of starch solution as an indicator. The thiosulphate solution is made by dissolving 24 grams of the crystallized salt in 1000 cc. of water, and standardized as follows: 3.8657 grams of potassium dichromate is dissolved in 1000 cc. of water. 20 cc. of this solution is added to 10 cc. of a 10 per cent potassium iodide solution and 5 cc. hydrochloric acid. Since each cc. of the dichromate solution liberates exactly 0.01 gram iodine, altogether 0.2 gram iodine will be liberated. This is titrated with the thiosulphate solution and its equivalence calculated in terms of iodine. The iodine value is reported as the centigrams of iodine absorbed per gram of resin. A blank determination must be run with each set of samples.

10. **Saponification number.**—1 gram of resin is dissolved in

a mixture of 25 cc. toluol and 25 cc. ethyl alcohol in a 300 cc. flask. 10 cc. of a 0.5N solution of potassium hydroxide in methyl alcohol is added with a pipette. The flask is fitted with a reflux condenser and the contents boiled on the steam bath for 45 minutes. Phenolphthalein indicator is added and the liquid titrated with a standard 0.3N aqueous solution of sulphuric acid. A blank determination is run with each set of samples. The saponification number is reported as the milligrams of potassium hydroxide per gram of resin. The original method (C. H. Wolff, "Die Natürliche Harze," Berlin, p. 33) calls for double these amounts, but we have found our determinations accurate enough and the smaller flasks more convenient when running many samples.

DAMAR RESENE CONTENT

11. **Per cent "wax."**—50 grams of the sample is dissolved in 50 grams of toluol. 50 grams of ethyl alcohol is added with stirring and the mixture covered and allowed to stand 24-48 hours. The liquid is decanted off, the lower part being filtered if feasible. The solid (wax) is dried over night at 110°-120°, weighed, its weight calculated to per cent wax, and which includes per cent of insoluble content of the particular grade of gum.

12. **Per cent beta-resene.**—2 grams of the sample is dissolved in 10 cc. of a 10 to 1 toluol-alcohol mixture and filtered. To the filtrate is added 100 cc. ethyl alcohol and the mixture allowed to stand over night. The precipitate is then filtered off, washed with a little 3:1 alcohol-toluol mixture, dried, and weighed. The weight is calculated as per cent beta-resene.

Solubility

13. **Solubility test.**—Equal portions of resin (100 grams) and solvent (100 grams) are mixed in a bottle, the bottle being turned continuously end for end at about 30 r.p.m. for 15-18 hours. In the determinations given under damar of the per cent of damar insoluble in certain solvents, the mixture was filtered with suction, the residue washed with one portion of solvent, dried, and weighed. As this method is not applicable in the case of less readily soluble resins, it is recommended that the solubility samples be allowed to stand several days, then the more or less clear liquid decanted and the wet residue weighed.

Solubility is to be reported as S or soluble (1-10 per cent residue), LS or largely soluble (10-50 per cent residue), PS or partly soluble (50-75 per cent residue), SLS or slightly soluble (more than 75 per cent residue), Sw or swelled but undissolved, TVJ or transparent viscous jell, GL or gelatinous liquid, I or insoluble (resin unattacked by solvent).

VARNISH TESTS

14. **Cold water test.**—See page 33.

15. **Color.**—Reported as numbers on a comparison scale devised by Gardner and widely used, consisting of 18 solutions of ferric chloride, some with small additions of other salts, varying in color progressively from 1 (nearly water white) to 18 (matching the color of a solution of 3 grams of potassium dichromate in 100 cc. of sulphuric acid).

16. **Exposure.**—See page 34.

17. **Flexibility and adhesion.**—The varnish or lacquer is poured on a 3.8 x 11.7 cm. panel of thin gauge tin-coated steel sheet. After drying, the panel is bent on a rod of 2 mm. radius and the relative flexibility and adhesion judged from the appearance of the film at the bend.

17-a. **Toughness.**—Metal panels used shall conform to ASTM D 154-28, paragraph 10: "Test panels shall be cut from bright tin plate weighing not more than 25 grams nor less than 19 grams per square decimeter (0.51 to 0.39 lb. per square foot). It is important that the tin plate shall be within the limits prescribed. The panel shall be about 7.5 x 13 cm. (3 x 5 in.) and shall be thoroughly cleaned with benzol immediately before using.

> Note: Commercial No. 31 gauge bright tin plate should weigh about 0.44 lb. per sq. ft. It is important that the rags used in wiping the panels are clean."

Cleaned panel shall be dipped vertically into the paint sample to a depth of four inches, immediately withdrawn, and allowed to hang in a vertical position at room temperature.

From 20 to 24 hours after panel prepared as above has been dipped, bend it rapidly through 180° around a one-eighth inch diameter rod, the line of bend being at right angles to the panel

length and at the middle of the painted area. Examine carefully for cracking, using a hand lens. Any cracks whatsoever shall be considered as failure.

18. **Gas proofness.**—See page 34.

19. **Gloss.**—The varnish or lacquer is poured onto a panel coated with a flat white enamel ("flat" means dull finish). After thorough drying, the panel is set up five feet from and facing a negative full size photograph of an optical chart of the common type containing lines of type of decreasing size. The lines of type are numbered 1 to 11, No. 1 being the largest. The relative gloss of the film is reported as the number of the smallest line of type legible in the reflection of the chart in the panel when the observer's eye is held 15 to 20 cm. from the panel. For other details, see page 33 of this booklet.

20. **Hardness.**—The use of lead pencils of different hardnesses to determine the scratch hardness of films (for details, see page 33) has been abandoned in favor of the Sward hardness rocker which, although still not overly satisfactory, is somewhat more precise. This instrument is a pair of circular rockers with a pendulum pivoted at the top between the rockers. The rockers are flat bronze rings 10.2 cm. in diameter and spaced 2.5 cm. apart. The edges of the rockers are semi-circular in cross section with a radius of 0.5 mm. The pendulum is mounted in pivot bearings at the top, is 8.7 cm. long, and terminates in a pointer which swings across a scale as the rocker oscillates. The scale is marked at the point where the rocker completes its fiftieth complete oscillation on glass. The varnish is poured onto a small glass panel. After the proper drying time, the panel is placed in a level position and the rocker set on it. The rocker is rolled to the left until the pendulum touches a stop on the rocker, then released. The number of swings made by the rocker until the pendulum first fails to swing beyond the mark on the scale mentioned above is counted. This number multiplied by two gives the hardness value.

21. **Kauri reduction.**—See page 34.

22. **Panels for exposure tests.**—For details of maple and redwood panels, their preparation and coating, see page 32 of this booklet.

23. **Photomicrographs of exposed panels.**—See page 34.

24. Viscosity.—Viscosity of solutions and varnishes is determined by the Gardner-Holdt air bubble method which is more or less standard in the industry. Liquids (mineral oils) of previously determined viscosity sealed in glass tubes 10.75 mm. in diameter and approximately 11 cm. long, are used as standards. These standards are widely known and used in this country. They are designated by letters, "A" being the least viscous. The liquid of unknown viscosity is poured into a tube of the same diameter and length and the tube corked, leaving an air space approximately the same size as that in the standard tubes. Unknown and standards are brought to 25° C. and then held side by side in a vertical position. The viscosity of the sample is reported as that of the standard whose bubble moves at the same rate as the bubble in the sample tube.

ABSOLUTE VISCOSITIES CORRESPONDING TO BUBBLE VISCOSITIES

A 0.50	L 3.00	W 10.70
B 0.65	M 3.20	X 12.9
C 0.85	N 3.40	Y 17.6
D 1.00	O 3.70	Z 22.7
E 1.25	P 4.00	Z1 .....27.0
F 1.40	Q 4.35	Z2 .....36.2
G 1.65	R 4.70	Z3 .....46.3
H 2.00	S 5.00	Z4 .....63.4
I 2.25	T 5.50	Z5 .....98.5
J 2.50	U 6.27	Z6 148
K 2.75	V 8.84	

PROPERTIES AND APPLICATIONS OF DAMAR

The damar resins constitute a class of natural resins of considerable commercial importance. Damar is used industrially in the preparation of surface finishes, oil varnishes, lacquers (usually after a dewaxing operation, the details of which see), flatting varnishes, coatings of the solution type which take advantage of the solubility of damar in cheap petroleum solvents, printing inks of various types and ranges of plasticity and fluidity, transparent varnishes, paints, linoleum and related materials, some types of plastics, rubber compositions, molding compounds, pyrotechnic materials and fireworks, adhesives, and additions to dry colors and pigment pastes.

Damar is produced in the Malay States and is known in commerce under the name of Singapore Damar, but most of the supplies of the United States come from the Dutch East Indies, which variety is marketed under the name of Batavia Damar. The word "damar" in the Malay States and the East Indies originally referred to a torch made by mixing leaves and bark with the powdered resin. These "damar" torches lighted the paths during travel through the jungle forests.

Damar resin is an exudation from a number of species of trees of the Dipterocarpaceæ family of the Hopea and Shorea species, appearing when the tree is wounded either accidentally or by tapping. Two varieties are at present offered for sale in the United States—Batavia and Singapore. These take their names not from their places of origin, but from the place where they are graded and exported. In the United States market the term "damar" is confined to the soft spirit-soluble type of resin, which has been gathered within a short time after its exudation from the tree. The fossilized resins from the same source, also called damar in the Dutch East Indies, are termed "East India Resins" in this country. These resins are all collected in Java, Celebes, and adjacent islands, Sumatra, and Borneo in the Dutch East Indies.

The companies engaged in gathering, sorting, and exporting damar have organized the Nederlandsch Indische Vereeniging voor den Handel in Gommen (Netherlands Indian Gum Association), which with the very active support of the Dutch East Indies government, is providing for the standardization

of the resin exported by closely supervising collection and sorting, and is carrying on an extensive research program with the object of improving the quality of the resin and obtaining still greater uniformity, to improve present industrial applications, and to find new uses.

In contrast to the Manila resins which show solubility in alcohol, and insolubility in coal tar solvents, the damars are characterized by their solubility in coal tar hydrocarbons such as benzol, toluol, and xylol, and in petroleum hydrocarbons such as V. M. and P Naphtha, varnolene, and hydrogenated naphthas, and partial or little solubility in alcohol, either pure or denatured.

In experimental plantations in the Dutch East Indies methods of tapping and collecting are being studied. At the Laboratorium voor Scheikundig Onderzoek at Buitenzorg, Java, a detailed study is being made of the physical and chemical properties of the resins obtained from the various species of damar-producing trees, with a view to encouraging the cultivation of those varieties producing the most useful resin. The investigation of the industrial applications of damar to date has involved the testing of some thirty-two different samples of commercial damar of various grades to determine physical and chemical characteristics, such as melting point, acid number, specific gravity, non-resinous contaminants, and moisture content, etc., and to obtain some idea of their relative technical usefulness.

PROPERTIES OF DAMAR

Some fifty-five species of damar-producing trees have been botanically catalogued by the Laboratorium voor Scheikundig Onderzoek, but the supervision of collecting and sorting enforced by the Dutch East Indies government has resulted in such uniformity in the exported resin that two damar samples of the same grade seldom show variations of more than one or two points in such characteristics as acid number, iodine number, melting point, etc. Damar resin varies in color from a strong yellow to almost water-white, generally clear or only slightly opalescent. It is characterized by having the lowest acid number of any important natural resin, this value rarely exceeding 37 or 38 and in commercial samples generally running from about 25 in the best grade to about 35 in the poorest. Its melting point by the mercury method (M. Rangaswami, Journal of the Oil and Colour Chemists' Association, vol. 13, p. 287 (1930)) varies from 100° to 110° C., moisture content from 0.5 to 1.5 per cent.

In Singapore the damar is sorted into three grades on the basis of color and freedom from impurities, number 1 being the lightest in color and most transparent. Numbers 2 and 3 are less transparent and have some color. Reference should be made to page 9 of this booklet for the commercial grades of Singapore Damar. In Batavia the resin is scraped free of surface dirt, then assorted by sieving according to size into seven grades. Damar A is that grade retained on an A screen having a 0.588 inch opening, smaller sizes being designated by letters down to grade F, which passes through a 40 mesh screen. The seventh grade, Dust, is composed of very finely divided material, mostly obtained from the scraping operations. As a general trend the color and amount of impurities in the resin increase with decreasing size. The A grade contains about 0.1 per cent non-resinous matter, the B, C and D grades but slightly more, while the F grade may contain 3.5 per cent and the Dust 4 to 6 per cent.

Reference should be made to page 10 of this booklet for the commercial grades of Batavia Damar and for the specifications of the grading screens, and to pages 6 and 7 for the origin, type, and weights of damar packages.

Where standard Batavia Damar screens are not available,

the following screens according to an American specification are suggested as giving approximately the same results. All of these screens have square holes.

A—made of .162 in. diameter wire spaced ¾ in. center to center, so that the screen has an opening .588 in. wide.

B—a screen made of wire .054 in. in diameter, 3 square holes per inch, so that the opening is .279 in.

C—a 6-mesh screen having 6 square holes per inch made of wire having a diameter of .041 in. and a screen opening of .126 in. width.

D—a 10-mesh screen having 10 square holes per inch made of wire of a diameter of .035 in., the screen openings being .065 in.

E—a 40-mesh screen made of brass wire cloth of wire .012 in. diameter and a screen opening of .013 in.

Tschirch and Glimann (Archiv der Pharmazie (1896) page 585) and Zinke and Unterkreuter (Monatsheft. (1918) p. 865; Pharmazeutische Monatshefte (1905), p. 105) have established that, besides two or three per cent of essential oils of terpenic nature, damar is composed of two resin acids and two resene compounds. The resin acids may be readily separated from the resenes by extraction with hot dilute sodium hydroxide solution, from which the resin acids may be precipitated by the addition of mineral acid. The two resenes may be separated by extraction with ethyl alcohol, in which the alpha-resene dissolves, leaving the beta-resene as a residue.

Commercial grades of damar have been compared with one another in their solubility in various solvents. The solubility, as indicated by the viscosity of the solutions, varied but little from one grade to the other. The viscosity of the lowest grade seldom exceeded that of the highest grade by more than 0.5 poise in a 1:1 solution. The lower grades, as was to be expected, gave somewhat more cloudiness than the higher. Table I gives the solubility of damar in most of the common types of solvents, Table II its solubility in a number of trademarked petroleum solvents. Damar is completely soluble in chloroform, carbon disulphide, benzaldehyde, hydrocarbons, coal tar solvents, and largely soluble in esters. These solvent types are additional to those in the tables. While damar is only partially soluble in alcohol, it is soluble in mixtures of alcohols and hydrocarbons or esters.

TABLE I. SOLUBILITY OF DAMAR RESIN IN COMMON ORGANIC SOLVENTS

A. Solvents dissolving Damar completely.

Solvent	Damar Solution (1:1) *Clarity	**Viscosity
Amyl Acetate	c	A
Amyl Alcohol	c	K
Aniline	a	gel
Benzol	b	A
Butyl Acetate	b	A
Carbon tetrachloride	b	Z 2
Chlorbenzol	a	A
Dipentene	a	B
Ethyl Ether	b	A-
Furfural	a	E
"Hercosol No. 80" (terpene hydrocarbons & ketones)	a	C
Isopropyl ether	b	A-
Methyl Salicylate	a	I
Nitrobenzol	a	gel
Octyl Acetate	a	B
Tetrachloroethane	a	P
Tetralin	a	H
Toluol	b	A-
Turpentine	b	K

B. Solvents dissolving Damar partially.

Solvent	Per cent of resin dissolved (approximate)
Acetic Acid (glacial)	60%
Acetone	70
Benzyl Alcohol	85
Butyl Alcohol	70
Butyl Carbitol	80
Butyl Lactate	85
Cellosolve	55
Cellosolve Acetate	75
Diacetone Alcohol	25
Dichloroethyl ether	75
Diethyl carbonate	85
Dimethyl Phthalate	40
Dioxan	85
Ethyl Acetate	80
Ethyl Alcohol (Formula SDI)	60
Ethyl Alcohol, anhydrous denatured (a)	65
Ethyl Alcohol, anhydrous denatured (b)	70
Hexalin	75
IsopropylAlcohol	85
Methyl Acetone	75
Methyl Acohol	55
Tricresyl Phosphate	50

*a—clear, b—cloudy, c—very cloudy.

**Viscosities are given on the Gardner-Holdt scale. Their equivalents in poises are as follows:

A—0.50 poise, B—0.65, C—0.85, E—1.25, H—2.00, I—2.25, K—2.75, P—4.00, Z 2—36.2.

TABLE II. SOLUBILITY OF DAMAR IN COMMERCIAL PETROLEUM NAPHTHAS

Refiner	Type of Naphtha	Distillation Range — Initial		Distillation Range — End Point		Damar Solution (1:1) — **Viscosity	Damar Solution (1:1) — *Clarity
A	1. Paraffins plus some naphthenes	60- 65°C	140-149°F.	92- 96°C.	198-205°F.	A—	b
	2. do	94- 99°	201-210°	118-122°	244-252°	A—	b
	3. do	115-120°	239-248°	138-143°	280-289°	A—	a
	4. do	163-166°	325-331°	198-200°	388-392°	C	a
	5. do	174°	345°	264°	507°	C	a
B	1. Hydrogenated petroleum (naphtha)	95°	203°	140°	284°	A—	b
	2. do	135°	275°	188°	370°	A—	a
	3. do	180°	356°	214°	417°	D—	a
	4. do	205°	401°	241°	466°	I	a
C	1. High Naphthenic content.	149-155°	300-311°	208°	406°	B	a
	2. Paraffin base	154-166°	309-331°	260-268°	500-514°	F	a
	3. do	149-154°	300-309°	207°	405°	B	a
	4. do	174-185°	345-365°	296°	565°	J	a
	5. do	149-155°	300-311°	207°	405°	B	a
	6. do	154-166°	309-331°	279°	534°	C	a
D	1. Paraffin base	88- 96°	190-205°	166-171°	331-340°	A—	a
	2. do	146-152°	295-306°	204-210°	399-410°	A—	a
	3. do	160°	320°	198°	388°	A	a
	4. do	177-188°	351-370°	277°	531°	D	a

*a—clear, b—cloudy.

**Gardner-Holdt viscosity standards used. Equivalents in poises are: A—0.50, B—0.65, C—0.85, D—1.00, F—1.40, I—2.25, J—2.50.

The important effect of the solvent on a damar solution should be given considerable attention by the user.

When viscosities of the 1:1 solutions (one part of resin to one of solvent on a weight basis) are compared, and the viscosities measured on the Gardner-Holdt bubble viscosimeter, it is found that the high solvency materials give solutions of low viscosity. Coal tar hydrocarbons and comparatively low boiling point petroleum hydrocarbons give solutions of low viscosity, of the order of 0.50 poise absolute viscosity. The hydrogenated petroleum naphthas give lower viscosities than do the straight paraffin naphthas. In the petroleum solvents, increase in distillation range means higher viscosities. The paraffins containing naphthenes are better solvents than the straight paraffins, as well as better than the higher distillation range hydrogenated materials. Terpenic type solvents give solutions of higher viscosity, while saturated cholorinated hydrocarbons, such as carbon tetrachloride, give very high viscosity solutions.

The alcohols are not useful as solvents, as they dissolve only a portion of the damar. Only a limited number of esters as simple solvents give complete solution. Nitrated hydrocarbons are very poor solvents and tend to give gels. Low molecular weight esters are poor solvents, higher molecular weight esters give solutions of low viscosity.

According to work reported by J. G. Davidson in Industrial and Engineering Chemistry, volume 18, page 669 (1926), damars are only partially soluble in the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and isoamyl ethers of ethylene glycol, and in the methyl, ethyl, and isopropyl ethers of propylene glycol. Damar is insoluble in glycol diacetate, diethylene glycol, triethylene glycol, and tetraethylene glycol, as well as glycol monoacetate. Damar is reported as being soluble in butyl propionate, and only partially soluble in glycol ether acetate, diethylene oxide, isopropyl acetate, propylene oxide, ethylene oxide, diethylene glycol monoacetate, and partially soluble in the ethyl ethers of diethylene glycol, triethylene glycol, tetraethylene glycol, and the butyl ether of diethylene glycol.

Additions of small amounts of other solvents may markedly affect the results given in the table, and small additions con-

siderably affect viscosity. A large amount of work in this direction is now being carried forward.

Experiments have shown that aside from greater color and cloudiness in the lower grades, clear varnishes and lacquers from the various grades show practically no differences. Hardness, flexibility, gloss, drying time, and tackiness of the film are practically the same for all grades. Grinding zinc oxide into spirit solutions of the resins gave enamels that were indistinguishable from one another.

Reference should be made to page 23 of this booklet for the properties of the commercial grades of Standard Batavia Damar. The saponification number of damar ranges from 30 to 39 for commercial samples. With the Hicks-Halphen test, damar shows a brown to lilac-brown color.

DEWAXING OF DAMAR

Damar resin is not completely compatible with lacquer solvents. Before being used in a nitrocellulose lacquer the resin must be treated by a process known as "dewaxing." This is essentially the removal of the beta-resene. The dewaxing process usually consists in dissolving the resin in a suitable solvent and precipitating the beta-resene or "wax" by adding ethyl or methyl alcohol, or mixtures of these as in denatured alcohols. Various extraction methods have been proposed and carefully investigated as well as operated on a semi-commercial scale. Difficulties minor or major in extent, of a chemical or a mechanical nature, have usually interfered. In general, users of damar do their own dewaxing, although dewaxed damar solutions may be obtained. The precipitation method remains the only one in wide use. The nature of the solvent used and the grade of damar both affect the character of the precipitate obtained. The effect of the solvent on the viscosity of the solution has been discussed above.

For the better grades of damar, the best results are obtained by following the widely used procedure of dissolving the resin in an equal weight of toluene and adding an equal weight of alcohol. For the poorer grades, however, the toluene is better replaced by a mixture of two-thirds light petroleum naphtha and one-third ethyl acetate, or by ethyl acetate 12.5 per cent, acetone 12.5 per cent, and benzene 75 per cent. By increasing the proportion of damar to as much as two and a half parts, the toluene procedure may be made to give good results with all grades of damar. The wax-free solution is of low viscosity, about 0.5 poise (A on the Gardner-Holdt scale) and because of its low solvent content—about 45 per cent—is adaptable to a wider variety of lacquer formulations.

The actual beta-resene content of damar resin varies from 8 per cent to 11 per cent. Generally in dewaxing damar there is a total loss of 15 to 20 per cent, as some of the solution is occluded in the precipitate.

The dewaxed damar is soluble, or mostly soluble, in nearly all the common organic solvents.

A very desirable method of dewaxing damar would involve

an extraction or percolation procedure. Dewaxing experiments have been made using the following proportions of resin, aromatic solvent, and alcohol. The damar was dissolved in the coal tar solvent and the alcohol added with stirring. These proportions of solvents form constant boiling mixtures in each case.

Batavia Damar	Aromatic Solvent	Alcohol
1. 20 grams	20 grams benzol	13.5 grams methyl alcohol
2. 20 "	20 " "	9.5 " ethyl alcohol
3. 20 "	20 " "	11.5 " isopropyl alcohol
4. 20 "	20 " toluol	46.5 " ethyl alcohol
5. 20 "	20 " "	45. " isopropyl alcohol

Numbers 4 and 5 gave much the best separation of wax from wax-free resin.

Samples of crushed damar were extracted in a Soxhlet extractor using a constant boiling mixture composed of 46 cc. toluol and 112 cc. isopropyl alcohol. In one run the resin was placed in an ordinary paper Soxhlet thimble. In others the resin was wrapped in small pieces of cheesecloth, each package containing 10 to 15 grams of resin, and 3 to 4 such miniature sacks placed in the upper chamber of the extractor. A satisfactorily effective separation of wax from wax-free resin was obtained in each case.

It was desired to investigate the possibility of an extraction process of dewaxing to be used on the resin as received. A two-liter flask was fitted with a vapor outlet tube leading to a reflux condenser which emptied into a can from the bottom of which a siphon led back to the flask—in principle a large scale Soxhlet extractor. One hundred grams each of Damar B, C, D, and A/D were wrapped in separate cheesecloth packages and placed in the can. Four hundred sixty-three cc. of toluol and 1088 cc. of alcohol (a constant boiling mixture) were placed in the flask and boiled. When about 800 cc. of solvent had boiled over, the siphon emptied the liquid contents of the can into the flask. When this had occurred six times, the operation was stopped and the resin examined. The beta-resene which had

been separated in the outer layers of the packages was very pure, as indicated by its melting point of 203°. However, there was considerable unattacked resin. The following percentages of the original resin samples remained in each package.

Sample	Residue	Wax in Residue	Wax-free Resin in Residue
B	34.7%	10.6%	24.1%
C	47.3	12.5	34.8
D	44.7	12.4	32.3
A/D	39.4	10.4	29.0

From these results it would appear that an extraction process would require agitation to be very successful. Larger scale experiments are being carried forward as well as work with other mixtures of solvents.

DAMAR WAX

Damar wax is soluble in petroleum naphthas over a wide range of boiling points, whether these petroleum naphthas be of a paraffin base or a naphthenic base, or whether they be hydrogenated naphtha. The wax is also soluble in terpineol in which, however, the solutions are so viscous that gels are formed, and in turpentine. The wax shows solubility in coal tar solvents and tetralin.

It is insoluble or only slightly soluble in lacquer type solvents. In all the common organic solvents, the beta-resene or wax appears less completely soluble than the wax-free portions of the resin. Specifically, the wax is insoluble in alcohols of various types, and trade name materials such as Ansol M, Shellacol, and Solox of the denatured group, and also insoluble in isopropyl alcohol, butyl alcohol, amyl alcohol, diacetone alcohol, benzyl alcohol. The wax is insoluble in ethers and esters and a number of ketones as given here:

Dichlorethyl ether	Diethyl carbonate
Cellosolve	Butyl lactate
Butyl carbitol	Dimethyl phthalate
Ethyl acetate	Ethyl abietate
Butyl acetate	Acetone
Amyl acetate	Methyl acetone
Hexalin	Dioxan

The wax when purified to beta-resene by reprecipitation becomes a brittle white material of very low acid number (2-4), melting at 200° to 210° C. If cooked with linseed oil, it gives a clear product after being heated one-half hour at 300°. Twenty to 25 per cent of damar wax in linseed oil cooked at 300° for 45 minutes gives a product of a viscosity equal to that of the heaviest type of lithographic varnish. Used in cold cut varnishes and in enamel vehicles, it greatly increases their viscosity and materially reduces the gloss of the finish obtained. These properties suggest its possible use where non-reactivity, false body, or flat finish are desired.

A fairly pure sample of beta-resene was prepared by re-

precipitation (m. p. 195°). This sample was used in the following tests.

The influence of beta-resene on the gelation time of tung oil was investigated by heating test tubes containing tung oil with varying proportions of beta-resene at 246° C. until gelation occurred.

Per Cent Tung Oil	Per Cent Beta-Resene	Gelation Time at 246° C.
100	0	40 minutes
88.9	11.1	50 "
80.0	20.0	55 "
66.7	33.3	85 "
50	50	90 "

The influence of beta-resene on the viscosity of tung oil was studied by heating tung oil with varying amounts of beta-resene to 170° C. in 30 minutes and allowing to cool.

Tung Oil	Beta-resene	Viscosity	
		Gardner-Holdt	Poises
100 grams	0 grams	I	2.25
92 "	8 "	T	5.50
85 "	15 "	Y	17.6
80 "	20 "	Z3	46.3

Similar experiments were made with linseed oil and beta-resene, heating the batches to 260° in 50 minutes.

Linseed Oil	Beta-resene	Viscosity	
		Gardner-Holdt	Poises
100 grams	0 grams	A	0.50
85 "	15 "	M	3.20
72 "	28 "	Z2	36.2
60 "	40 "	Very viscous	

DAMAR IN CLEAR LACQUERS

In studying the value of damar in lacquers, two series of lacquers were made up, employing a resin-nitrocellulose ratio of 1 to 2 in the first series and a ratio of 1 to 1 in the second.

Throughout each series the formulation was the same for each lacquer except for the type of resin used. The resins used were: ordinary dewaxed damar, damar resin acids, alpha damar resene, ester gum, a commercial hard Manila ester containing some ester gum, two modified phenolic resins recommended for lacquers, and an alkyd type. In the laboratory tests the comparative values given by the one series were duplicated in the tests on the other series. Table III gives the results of tests carried out in these lacquers. It will be seen that the dewaxed damar ranks higher in these tests than any of the other resins except the alkyd type, which is of considerably higher cost. Curiously, the dewaxed damar gives materially better properties than either of the two fractions of the resin which compose it—the damar acids and the alpha damar resene.

Damar, unlike any of the synthetic resins used in these lacquers, is rapidly bleached by exposure to sunlight. The lacquers were poured on white coated panels and one-half of each panel exposed under glass to the sun for ten sunny summer days. There was no change in the color of the alkyd resin lacquer films, which were colorless from the start. The six lacquers containing damar resin fractions were all alike bleached to a water-white by the exposure. All the remaining lacquers, originally having a slight coloration, showed a very pronounced yellowing during the exposure.

TABLE III. TESTS ON CLEAR LACQUERS

Resin	Whiteness	Hardness	Resistance to water	Gloss	— Weathering Time — 1st Series	2nd Series
Dewaxed Damar	2*	1*	2*	All	18 weeks	20 weeks
Damar Acids	8	3	7	about	20 "	10 "
Alpha-Resene	4	5	6	the	10 "	7 "
Ester Gum	3	8	4	same	9 "	8 "
Manila Ester	6	4	1		9 "	8 "
Mod. Phenolic No. 1	5	6	5		9 "	9 "
Mod. Phenolic No. 2	7	7	3		9 "	8 "
Alkyd	1	2	8		26 "	29 "

*Numerals indicate comparative rank, number one indicating the best properties.

At present no processed damar is on the market and the non-resinous material present in the lower grades sometimes constitutes something of a nuisance to the user. Laboratory experiments have shown the entire feasibility of cleaning the resin by two different methods—melting, filtering under pressure, and casting into blocks; and dissolving in a solvent such as benzene, filtering and steam distilling off the solvent. In filtering the molten resin, a temperature of 160° C. and a pressure of 70 pounds per square inch are sufficient to effect a reasonably rapid filtration. The cast gum obtained is free from air holes and slightly darker than the original resin. The treatment lowers the melting point by 10 to 15°, but does not change the acid number. A low grade gum treated in this way gives solutions just as clear as does the best gum, although its solubility, as indicated by the viscosity of the solution, is not appreciably changed. In a spirit varnish film the filtered resin shows no change from the original in color or hardness, and exhibits a slightly better flexibility.

The solvent method gives a product with similar advantages over the original resin, with the additional one of involving a decrease rather than an increase in color. However, in order to remove the moisture from the steam distillation, it is necessary to pulverize the gum and dry it in air, giving a product less convenient to handle.

Damar resin, unlike other natural resins except its fossilized relatives the East India resins and rosin, can be dissolved in hot drying oils without pretreatment. When used alone with drying oils, it tends to give tacky and dull films. By blending with ester gum and phenol-formaldehyde resins, however, it has been found possible to obtain varnishes of good drying characteristics and gloss. These varnishes resist weathering quite well and the cheapness of damar may recommend it for this use, especially where its low acid number and its superiority in elasticity over ester gum may be of advantage.

PROPERTIES AND SOME APPLICATIONS OF EAST INDIA RESINS

The East India resins, the fossil damars, were originally sold in this country under a variety of names. Batu and Hiroe came from Macassar, Batu being yellow, brown, and black, Hiroe yellow-brown and red-brown. Batu was also imported from Borneo. The Hiroe came partly from the Moluccan Islands, partly from Borneo, that coming from Borneo being sometimes called Damar Rasak (C. van de Koppel, "De Handel in het Nederlandsche-Indische Copal (Manila-Copal) en het gebruik er van voor verschillende industrieele doeleinden," Buitenzorg, Java, 1929). Pale East India resins are now sold in this country as East India Macassar, which includes the old Hiroe grade, and East India Singapore, which includes the old Rasak grade. Batu is sold as before under its own name, and the Black resin known in the East Indies as Damar Hitam and commonly called here "Bold Black Scraped" is now sold as Black East India.

Batu finds employment in paints and varnishes, particularly as a flatting agent, in traffic marking paints and finishes, to some extent in adhesives, plastics, inks and oilcloth.

In a search for a cheap alkali-resistant ink varnish, a combination of Batu and tung oil has given some very favorable results. The Batu was run, then cooked with tung oil just enough to safely dissolve, then thinned with heavy petroleum thinner to the proper body. One batch of resin was run in an open kettle, another in a closed kettle, both heat treatments being a little more severe than is customary. The proportions of oil to resin used were 3 to 2 plus about 0.75-1.0 part of thinner, and 1 to 1 plus about 1-1.25 parts of thinner. The resin run in the closed kettle was found to impart slightly better alkali-resistance than the other, although both were good.

Batu is soluble in esters, petroleum hydrocarbons, and coal tar solvents. It is almost insoluble in alcohol, ether, and oil of turpentine.

Black East India finds application in dark colored varnishes, gloss paints, printing inks, plastics and oilcloth, and adhesives. Black East India varnishes when first applied are

quite dark in color, but rapidly bleach to transparent films comparable in color with varnishes made from very light resins.

Black East India resin is soluble in esters, petroleum hydrocarbons, and coal tar solvents; partly soluble in ketones, but insoluble in alcohol.

For the commercial grades of Batu and Black East India, reference should be made to page 11 of this booklet; for the characteristics, to page 22, and of the run gum, page 30; for varnishes, to page 36, 40, and pages following; for formulations, pages 61 to 64, in which Batu can be put in place of Black East India; and for blends with phenolics, pages 67 to 70.

The resins are sorted according to size into five grades: Bold (over 4 cm.), Nubs (2-4 cm.), Chips (1-2 cm.), Seeds (less than 1 cm.), and Dust. As in the case of the damars, the larger sizes are the cleaner. The melting points of these resins vary from 125° to 150° C., acid number 20 to 30. The solubility of these resins in the various solvents closely parallels that of the freshly exuded damars, but the solutions are cloudier and more viscous.

As with the damars, the East India resins can be separated by extraction with alkali into an acid and a resene fraction, but a much greater portion of the resin is insoluble in aqueous alkali than is the case with damar. As with the damars again, the East India resins can be separated into an alcohol-soluble and an alcohol-insoluble fraction. The alcohol-soluble fraction gives clear solutions in most organic solvents and its varnish film is glossy. The alcohol-insoluble fraction is insoluble in all but a few solvents and in those gives cloudy, viscous solutions, and its varnish film is dull.

For the commercial grades of the East India resins, reference should be made to pages 6 to 9 of this booklet; for characteristics, to pages 22 to 24; for solubilities, to pages 25 to 29; for run resin, page 30; for varnishes, pages 36 to 40 and pages following; for type formulations, pages 61 to 64, in which the East India resins can be put in place of Black East India; for blends with phenolics, pages 67 to 70.

The Pale East Indias find application in various types of varnishes, gloss paints, printing inks, sizing materials, plastics,

miscellaneous decorative and protective coatings, to some extent in lacquers, adhesives of miscellaneous compositions, color pastes, plasters, and wax compositions.

Pale East India resins are soluble in acetylene tetrachloride, benzol, toluol, xylol, ethyl ether, isopropyl ether, kerosene, carbon tetrachloride, chlorbenzol, tetralin, turpentine, dipentene, varnolene, linoleic acid. In most of these solvents, however, they form cloudy solutions. They are insoluble in ansol, butyl alcohol, denatured alcohols, isopropyl alcohol, methyl alcohol, acetone, cellosolve, cellosolve acetate, ethyl acetate, amyl acetate, dichloroethyl ether, acetic acid. In general, they are soluble in petroleum hydrocarbons and in coal tar solvents, yielding cloudy solutions; but they are practically insoluble in alcohols and esters.

While East India resins can be dissolved in drying oils without pretreatment, a more stable solution is obtained by first heat treating the resin. An extensive series of experiments reported to the public (C. H. Allen and K. M. Sprinkel, "Recent Developments in Natural Resin Varnish, II and III", Official Digest of the Federation of Paint & Varnish Production Clubs (1935), pages 54-66, 111-124; C. L. Mantell, C. H. Allen, and K. M. Sprinkel, "Research on Natural Resins and Their Varnishes," Official Digest of the Federation of Paint & Varnish Production Clubs (1936), pages 4-14) and referred to above in this booklet has shown that by employing already widely known methods of cooking the East India resins can be made to yield oil varnishes that compare favorably in all important properties with those obtained from other resins of a comparable price.

Important applications of East India resins are in the field of traffic marking paints. Manilas are also used for this purpose. Some sample specifications and formulae are given. The paints all have the characteristic that they must dry rapidly, stand traffic and not allow "pick-up," be readily applied, cover well, and not "run."
For example, New Jersey states:

> "The paint shall dry sufficiently within one-half (½) hour after application so there will be no pick-up under

traffice and thoroughly dry free from tackiness within one (1) hour after application."

The paint is to be composed of:

	Minimum Per cent	Maximum Per cent
Vehicle	39	41
Pigment:		
Inerts	30	32
Lithopone	55	60
Zinc oxide	10	12

The vehicle shall contain not less than 50 per cent of non-volatile material composed of fixed drying oils (tung or linseed or a mixture), driers, and gum varnish prepared from East India Batu gum; the remainder shall be volatile material.

Montana specifies for white heavy duty paint:

	Minimum Per cent	Maximum Per cent
Gum vehicle:		
*Gum (East Indian DBB)	35	37 (by wt.)
Solvent	63	65 (by wt.)
Composition of paint:		
Pigment	42	45 (by wt.)
Gum vehicle (as above) (shall be mill ground)	55	58 (by wt.)

* This terminology does not conform with that of the American Gum Importers Association who would refer to the gum here as Manila DBB.

The pigment is a precipitated product of titanium dioxide 24 to 25 per cent and barium sulphate 75 to 76 per cent, and the solvent is:

Raw tung oil (China wood oil)....15 per cent by volume
Normal butyl alcohol.....17 per cent by volume
Acetone .....34 per cent by volume
Denatured alcohol, formula No. 1.34 per cent by volume

The butyl alcohol, acetone and denatured alcohol shall be mixed and then the wood oil shall be added to form a clear solution at 70° F.

Missouri contributes another type as below:

"White Traffic Line Marking Paint Used on Asphalt Streets

Gum vehicle by weight)..... 58 per cent

made up as follows:

Alcohol	34 gal.	
Acetone	34 gal.	
Butanol	17 gal.	
Raw wood oil.....	15 gal.	
	100 gal.—	65 per cent
Manila copal gum...	375 lb. —	35 per cent
		100 per cent

Grind and mix in pebble mill.

Pigment Titanox..... 42 per cent

100 per cent"

Still another variety is given below from Montana.

"Gum vehicle (by weight)..... 58 per cent

Solvent naphtha ...	43 gals.	
Mineral spirits	43 gals.	
Raw wood oil.....	14 gals.	
	100 gals.—	65 per cent
Gum content—Pale East India Nubs (Macassar).....	375 lb. —	35 per cent
		100 per cent

Grind and mix in pebble mill—although the gum can be cut separately and mixed in any kind of mill.

Pigment Titanox ..... 42 per cent

100 per cent"

California calls for Manila DDB as below:

"Gum solution:

C. P. acetone	26¼ gal.
Butyl alcohol	14⅛ gal.
Specially denatured alcohol, formula No. 1	19¾ gal.
China wood oil	10$\frac{11}{16}$ gal.
Manila DBB Chips	276 lbs.

This makes a yield of 92 gallons.

Pigmentation:

Use 92 gallons of the above solution, add one gallon amyl acetate, 463 pounds of Titanox B.

This makes 100 gallons of the finished product."

Illinois is somewhat similar.

"White zone paint.

(a) Pigment (per cent by weight):

Titanium pigment	100%

(b) Vehicle (per cent by weight):

Raw tung oil	10 to 12
Normal butyl alcohol	10 to 12
Acetone	20 to 22
Denatured alcohol	20 to 22
Manila copal resin DBB	35 to 37

(c) Paint (per cent by weight):

Pigment	42 to 45
Vehicle	55 to 58
Moisture, if present, not more than	1.0 "

No attempt has been made to do more than give examples of specifications. Complete data may be obtained from the various highway or public works departments.

CHEMICAL AND PHYSICAL CHANGES IN CONGO RESINS DURING RUNNING

Congo is a fossil resin, named from its locality of origin, Belgian Congo in Africa. Practically the whole of the supply is obtained either from the ground or from water courses. The trees which yield the resin still exist, but the resin is the result of exudations many years ago. The chief sources are the numerous deposits from six inches to three feet below ground. The collecting and cleaning is of special concern to the Belgian Congo Colonial government. The resin enters commerce at Antwerp, Belgium, where most of the sorting and grading is done.

For the commercial grades of Congo, see pages 19 and 20; for properties of the resin, see page 22; of the run resin, page 30; for Congo varnishes, pages 30 to 52; for formulations, pages 55 to 57 and page 64; for blends with phenolics, pages 65 to 70 of this booklet.

Congo is the hardest of the commercial natural resins. It is the universal varnish resin, adaptable to a wide range of coating compositions of good durability, color, elasticity, weather resistance, and ease of application.

In its original form, Congo is insoluble in practically all solvents; in a few it swells to give a viscous apparently gel-like solution. After cracking or running, Congo is soluble in a wide range of solvents and compatible with drying oils. When finely ground and exposed to the air in thin layers at temperatures near those of steam for several days, Congo is converted into a form which shows alcohol solubility; ordinarily it is completely alcohol insoluble.

Natural resins are divided according to their age into recent and fossil types. The recent resins are obtained by tapping the trees and are an abundant annual crop. The exuded material contains resins and volatile oils. The hardness and oil solubility of the resin as it comes on the market depend partly on the extent to which the volatile oils have evaporated. Some types of recent resins, such as damars, dissolve readily in oils without preliminary treatment.

The fossil resins have been dug up after aging many years

under ground. The chemical changes and more complete elimination of volatile oils from them have produced harder resins which do not dissolve in drying oils until they have been given a preliminary heat treatment called "running" or "cracking." Congos, Kauris and the harder varieties of East Indias and Manilas are examples of this type (see pages 53 to 63).

After running, the fossil resins are among the most soluble of all types of varnish resins and their varnishes are stable even when thinned with the low priced straight paraffin type mineral spirits.

The work reported here is a study of the running of Hard Dark Amber Congo to show the time, temperature, and other conditions necessary to make it oil soluble. The methods of running were varied widely to show their effect on the process itself and on the properties of the run resin. Detailed observations of the appearance of the Congo throughout the entire course of each run were made. The observations recorded for Run No. 26 are given here as an illustration of the physical changes taking place and the appearance of Congo during running. These descriptions, together with the other data given below, are intended to be so complete as to enable a chemist who is acquainted with oils and general varnish work to successfully prepare oil soluble Congo resin without previous acquaintance with it.

The thermal processing of a resin is a step-like operation, to some extent a distillation during which volatile oils, terpenic in nature, are driven off, a softening of the resin, breaking down some of its components, the formation of spongy masses which with the evolution of considerable foam pass into a liquid soluble in oil. When the liquid is allowed to freeze, it becomes a resinous solid which can again be readily remelted without further change in composition or properties.

It is important to note a few of the criteria of well run resin. Original resin and partially run resin will show noncompatability with drying oils. This incompatibility may be evidenced by insolubility, or by apparent solubility and precipitation on cooling or on standing. Original resin or incompletely run material will show insolubility with thinners such as coal tar solvents, petroleum solvents, or terpenic type solvents; run

resin will show ready and complete solubility. Incompletely run resin may show apparent solubility with drying oils and later precipitation after thinning with solvents.

Varnish makers often run to a "clean drip from the paddle," the paddle being a wide stirring stick or enlarged version of a spatula, and the resin appearing like a thin, homogeneous, hot oil.

Hard Dark Amber Congo has been run at temperatures from 400° to 700° F. (205° to 371° C.) in open and closed kettles with fixed and with variable losses in weight. Detailed descriptions of the methods used and of the appearance of the Congo throughout the process of running are recorded. Acid numbers, softening and melting points, and solubility in five solvents are given for the run Congos.

Kettles and Types of Runs

One-gallon heavy walled chrome-nickel kettles 6½ inches in diameter and 9 inches deep were used. The kettles were fitted with removable covers having a drip ring to return the condensate to the kettles without running down its overheated sides. In the cover were thermometer and funnel holes and a larger opening for stirring which had a closely fitting, easily removable lid.

Heating, cooling, and other details of the process were carried out as shown by experience to give results closely duplicating factory conditions.

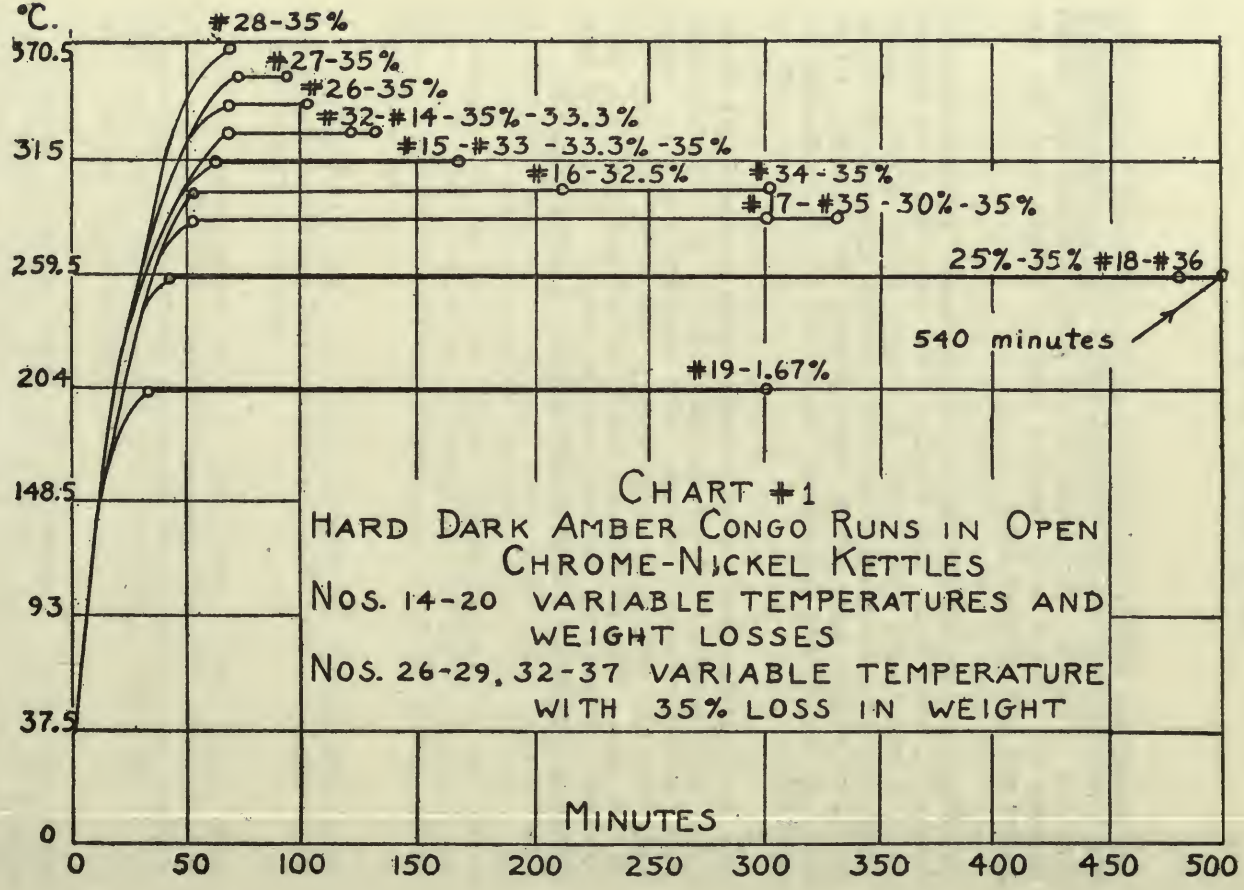
Six hundred gram lots of Hard Dark Amber Congo were heated to raise the temperature approximately 5.5° C. per minute until the intended maximum temperature was reached. This was held until the run was completed after which the resin was poured out to cool.

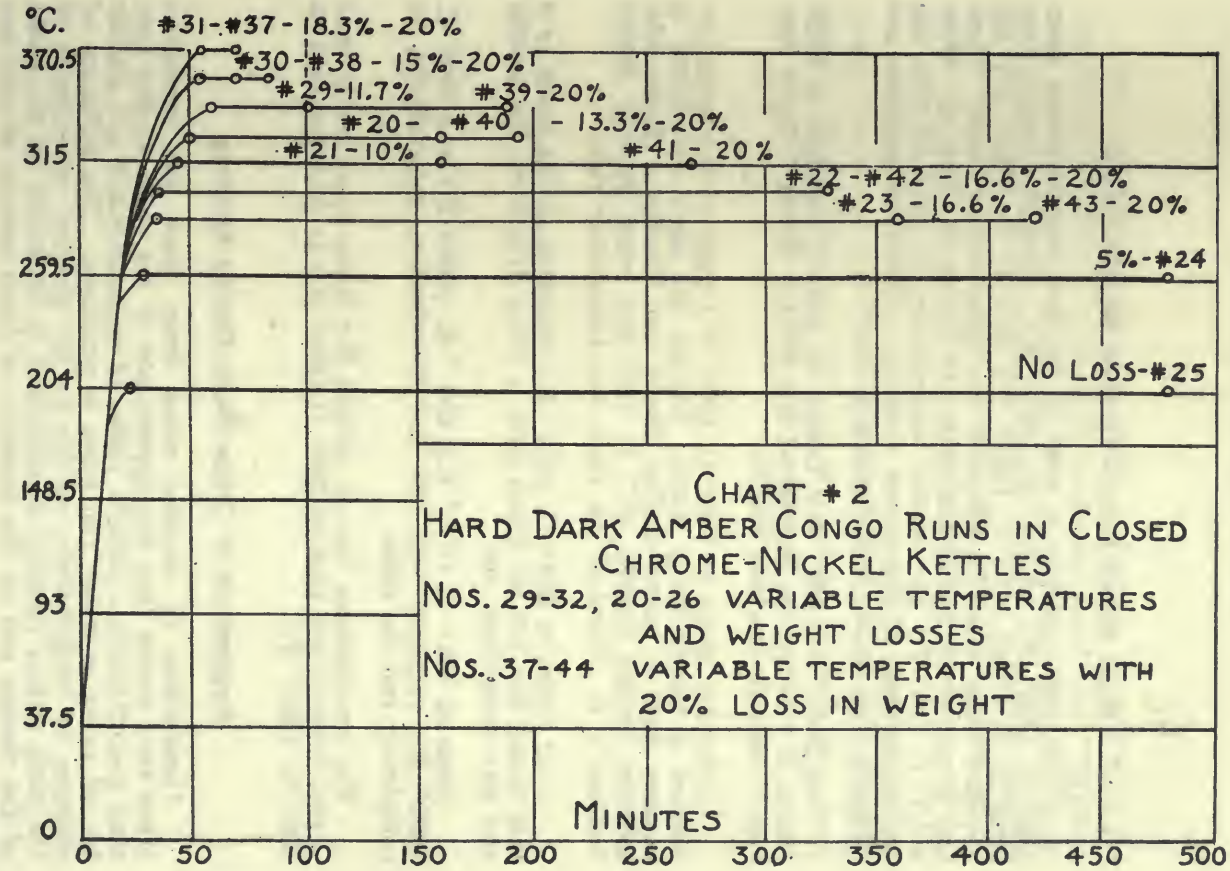
During running, "copal oil" is formed. When resins are run in "open kettles" without a cover, the copal oil vapors easily escape, a relatively great loss in weight results, and the

run resins are relatively hard. If run in a "closed kettle" with the cover on, the higher boiling copal oil fractions condense and are retained. Since these are good solvents the resins become oil soluble with smaller loss in weight and the run resins are not quite so hard.

The copal oil distillates (T. Hedley Barry, "Natural Varnish Resins," Ernest Benn, Ltd., London, 1932, page 40) from various natural resins have been found to contain water, pinene, dipentene, and other terpenes, and formic, acetic, and succinic acids. Research studies have given evidence that the presence of free copal oil in the run resin is an important aid in increasing its solubility.

Four series of run Congos were made in which the maximum temperatures varied from 205° to 371° C. The two open kettle series consisted of runs with variable losses in weight and with the maximum temperature held until the loss was 35 per cent. The two closed kettle series included runs with variable and with 20 per cent loss in weight. Time and temperature curves for the runs are given in Charts 1 and 2.


°C.
370.5
315
259.5
204
148.5
93
37.5
0
#28-35%
#27-35%
#26-35%
#32-#14-35%-33.3%
#15-#33-33.3%-35%
#16-32.5%
#34-35%
#17-#35-30%-35%
25%-35% #18-#36
540 minutes
#19-1.67%
CHART #1
HARD DARK AMBER CONGO RUNS IN OPEN CHROME-NICKEL KETTLES
NOS. 14-20 VARIABLE TEMPERATURES AND WEIGHT LOSSES
NOS. 26-29, 32-37 VARIABLE TEMPERATURE WITH 35% LOSS IN WEIGHT
MINUTES
0
50
100
150
200
250
300
350
400
450
500


°C.
370.5
315
259.5
204
148.5
93
37.5
0
#31-#37 - 18.3% - 20%
#30-#38 - 15% - 20%
#29-11.7%
#39-20%
#20- #40 - 13.3% - 20%
#21 - 10%
#41 - 20%
#22 - #42 - 16.6% - 20%
#23 - 16.6%
#43 - 20%
5% - #24
No Loss - #25
CHART #2
HARD DARK AMBER CONGO RUNS IN CLOSED CHROME-NICKEL KETTLES
NOS. 29-32, 20-26 VARIABLE TEMPERATURES AND WEIGHT LOSSES
NOS. 37-44 VARIABLE TEMPERATURES WITH 20% LOSS IN WEIGHT
MINUTES
0
50
100
150
200
250
300
350
400
450
500

Open Kettle Runs—Variable Weight Losses

This series consists of runs 19 to 14 at temperatures from 205° C. (400° F.) to 330° C. (625° F.). Constant weight loss runs 28 to 26 at 344° C. (650° F.) to 371° C. (700° F.) are grouped with them to complete the temperature scale. Time and temperature curves for them are shown in Chart 1. With a 5.5° C. (10° F.) per minute temperature rise for all runs the earlier portions of the curves coincide. The latter portions are straight lines at the temperature of the run.

At 205° C. (400° F.) Congo is merely softened a little where it touches the bottom of the kettle. After 1.7 per cent loss it came to constant weight.

After 2½ hours at 260° C. (500° F.) most of the resin had become a foamy waxy mass. During the next five hours it became first a heavy bodied liquid and finally a liquid like medium bodied linseed oil. It still had some spongy lumps floating in it. None of the resin was completely run.

Four hours at 288° C. (550° F.) changed all the resin to a thin liquid like hot oil which gave a clean drip from the paddle and was completely run.

Runs at 302° C. (575° F.), 315 ° C. (600° F.) and 330° C. (625° F.) required 160, 105 and 65 minutes, respectively, to completely run the resin.

The percentages loss in weight for these open kettle runs varied from 25 per cent at 260° C (500° F.) to 33.3 per cent at 330° C. (625° F.).

Appearance of Congo Resin During Running

Comparison of detailed notes from these and numerous other runs shows that the appearance of the resin during running goes through a definite series of changes which are similar for all cases in which run resin is produced. The influence of changes in temperature, so far as the general appearance of the resin during running is concerned, is primarily on the speed of the change and on the quantity of foam present at any one time.

The descriptions given in Table I. for Run 26 will hold for equivalent conditions in all of the runs discussed here. In large scale running the resin passes through the same stages. Since in commercial practice the running is carried to various degrees to adapt the resin to specific uses, the final appearance of the run resin will vary with the character of the run.

To give a "clean drip from the paddle," both liquid and paddle must be hot. The liquid should run off the paddle in smooth, free drops like thin hot oil and be entirely free from any ropy, lumpy or stringy appearance.

TABLE I.

Description of an Open Kettle Congo Run at 344° C. Which Was Held Until Oil Soluble. RR No. 26.

Time in Minutes	Temperature °C.	Temperature °F.	Appearance of Resin
5 to 10	100–150	212–302	Very small amount of smoke evolved.
15	200	392	Resin softening a little in bottom of kettle.
20	225	437	Much smoke. Part of resin becoming spongy.
25	250	482	Able to stir resin for first time. Both spongy and hard lumps.
30	270	518	Spongy lumps. Able to stir more easily; much smoke; beginning to foam.
35	290	554	Spongy lumps. Foam now doubles original volume of resin.
40 to 45	305–320	581–608	Spongy lumps. Foam increasing slowly.
50 to 60	330–340	626–644	Spongy lumps decreasing. Foam now triples original volume.
65	344	651	Very few spongy lumps remain. Foam down to double volume.
70	344	651	Spongy lumps all gone. Liquid now only equals original resin volume. Liquid is like much over-bodied china wood oil.
75	344	651	Foam nearly all gone. Liquid about like a 50:50 mix of over-bodied china wood oil and medium bodied linseed. Loss in wt. 21½ per cent.
90	344	651	Liquid does not quite give a clean drip from paddle—is about like medium bodied linseed oil. Loss in wt. 30 per cent.
100	344	651	Clean drip from paddle. Liquid is like thin bodied linseed oil. Resin is now completely soluble in oil. Loss in wt. 35 per cent.

Open Kettle Runs—35 Per Cent Loss in Weight

In this series, the maximum temperature varied from 260° C. to 371° C. (500° to 700° F.). All runs but that at 260° C. produced oil soluble resin. The times at maximum temperature varied from 0 to 371° C. (700° F.), to 6½ hours at 288° C. (550° F.). The physical and chemical properties of these and other run resins and their solubilities in several solvents are given in Tables II and III.

Examination of Tables II and III shows the important effect of the solvent on the viscosity of the resultant solution. This state of affairs has been previously commented on in connection with damar. Note that varnolene gives relatively high viscosity solutions, that those made with hydrogenated naphthas are appreciably lower, that coal tar solvents such as toluol are still lower, and butyl acetate gives very thin solutions.

TABLE II. PHYSICAL AND CHEMICAL PROPERTIES OF CONGOS RUN IN OPEN KETTLES

R.R. No.	Max. Temp. of run °C.	Per Cent Resin Loss	Softening Pt. °C.	Melting Pt. °C.	Direct Acid No.	Indirect Acid No.	Solutions (1 to 1 by wt.) Solubility—Viscosity														
							Varnolene			Hydrogenated Naphtha			Toluol			Butyl Acetate			N-Butanol		
								G. H.°	Viscosity Poises		G. H.°	Viscosity Poises		G. H.°	Viscosity Poises		G. H.°	Viscosity Poises		G. H.°	Viscosity Poises
Hard Dark Amber Congo run to a clean drip—Variable loss in weight.																					
HDAC			100	200**	70.1**	111.7	I			Sw			Sw			Sw			Sw		
CRC			95	140	76.0	83.7	PS-Sw			S	O	3.70	S	R	4.70	S	C	0.85	S	K	2.75
19	205	1.7	108	185**	76.6**	106.0	I-PSw			Sw			Sw			Sw			Sw		
18	260	25.0	104	148	75.4	79.7	S	X	12.90	S	P	4.00	S	H	2.00	S	E	1.25	S	T	5.50
17	288	30.0	92	150	78.4	83.6	PS-Sw			S	T	5.50	S	L	3.00	S	G	1.65	S	U	6.27
16	302	32.5	106	148	69.4	75.2	S	W	10.70	S	J	2.50	S	F	1.40	S	C	0.85	S	S	5.00
15	315	33.3	110	150	70.7	75.7	S	W	10.70	S	O	3.70	S	G	1.65	S	C	0.85	S	R	4.70
14	330	33.3	94	148	75.4	80.8	S	U	6.27	S	J	2.50	S	E	1.25	S	B	0.65	S	S	5.00
Hard Dark Amber Congo run to a constant loss in weight.																					
28	371	35	102	145	57.7	64.0	S	J	2.50	S	F	1.40	S	A	0.50	S	A	0.50	S	N	3.40
27	357	35	100	145	60.6	66.2	S	M	3.20	S	E	1.25	S	B	0.65	S	A	0.50	S	O	3.70
26	344	35	108	154	70.7	75.2	S	P	4.00	S	F	1.40	S	B	0.65	S	B	0.65	S	I	2.25
32	330	35	110	158	67.1	72.9	S	S	5.00	S	J	2.50	S	C	0.85	S	B	0.65	S	R	4.70
33	315	35	110	155	67.1	72.9	S	W	10.70	S	L	3.00	S	E	1.25	S	D	1.00	S	Q	4.35
34	302	35	105	160	59.4	66.2	S	T	5.50	S	K	2.75	S	C	0.85	S	C	0.85	S	Q	4.35
35	288	35	105	166	68.8	74.0	S	V	8.84	S	P	4.00	S	F	1.40	S	D	1.00	S	T	5.50
36	260	35	115	170	65.3	70.2	S	V	8.84	S	T	5.50	S	H	2.00	S	E	1.25	S	Q	4.35

Runs 26, 27, 28 complete the temperature range for each series.

HDAC—Hard Dark Amber Congo—not run.

CRC —Commercial Run Congo.

**—Average of several determinations.

*—Letters correspond to Gardner Holdt Viscosity Tubes.

TABLE 31. PHYSICAL AND CHEMICAL PROPERTIES OF CONGOS RUN IN CLOSED KETTLES

R.R. No.	Max. Temp. of run °C.	Per Cent Resin Loss	Softening Pt. °C.	Melting Pt. °C.	Direct Acid No.	Indirect No. Acid	Solutions (1 to 1 by wt.) Solubility—Viscosity													
							Varnolene			Hydrogenated Naphtha			Toluol			N-Butanol			Butyl Acetate		
								Viscosity			Viscosity			Viscosity			Viscosity			Viscosity	
								G. H.*	Poises		G. H.*	Poises		G. H.*	Poises		G. H.*	Poises		G. H.*	Poises
Hard Dark Amber Congo run to a clean drip—Variable loss in weight.																					
25	205		110	215**	67.7**	114.0	I-PSw			Sw			Sw			Sw			Sw		
24	260	5.0	110	220**	67.7**	88.7	PS-Sw			Sw			Sw			Sw			Sw		
23	288	16.6	102	148	73.6	76.8	S	U	6.27	S	I	2.25	S	C	0.85	S	B	0.65	S	N	3.40
22	302	16.6	102	145	70.7	75.7	S	R	4.70	S	H	2.00	S	C	0.85	S	B	0.65	S	N	3.40
21	315	10.0	94	135	80.8	86.9	S	S	5.00	S	K	2.75	S	D	1.00	S	B	0.65	S	H	2.00
20	330	13.3	85	128	64.8	68.4	S	L	3.00	S	E	1.25	S	A	0.50	S	A—	0.50	S	I	2.25
29	344	11.7	85	126	67.7	73.0	S	H	2.00	S	E	1.25	S	A	0.50	S	A—	0.50	S	G	1.65
30	357	15.0	85	128	63.0	79.0	S	F	1.40	S	C	0.85	S	A	0.50	S	A—	0.50	S	G	1.65
31	371	18.3	80	115	61.1	71.8	S	E	1.25	S	B	0.65	S	A	0.50	S	A—	0.50	S	F	1.40
Hard Dark Amber Congo run to a constant loss in weight.																					
43	288	20	95	143	65.3	70.2	S	O	3.70	S	F	1.40	S	A	0.50	S	A	0.50	S	L	3.00
42	302	20	85	140	55.8	61.7	S	H	2.00	S	C	0.85	S	A—	0.50	S	A—	0.50	S	Q	4.35
41	315	20	75	128	68.8	74.0	S	H	2.00	S	C	0.85	S	A—	0.50	S	A—	0.50	S	G	1.65
40	330	20	70	108	32.6	47.2	S	A	0.50	S	A—	0.50	S	A—	0.50	S	A—	0.50	PS-Sw		
39	344	20	70	104	42.8	51.6	S	A	0.50	S	A—	0.50	S	A—	0.50	S	A—	0.50	S	C	0.85
38	357	20	75	110	46.3	53.8	S	B	0.65	S	A—	0.50	S	A—	0.50	S	A—	0.50	PS-Sw		
37	371	20	85	110	55.2	66.2	S	C	0.85	S	A	0.50	S	A	0.50	S	A—	0.50	S	G	1.65

**—Average of several determinations.

*—Letters correspond to Gardner Holdt Viscosity tubes.

Closed Kettle Runs—Variable Loss in Weight

These runs were similar to those in the open kettle series. At 205° C. (401° F.) there was no loss in weight and after eight hours the resin was almost entirely unchanged. After seven hours at 260° C. (500° F.) with 5 per cent loss in weight, a spongy waxy mass remained which was much less nearly run than the open kettle run at 260° C. with 25 per cent loss. Runs 20 to 23, inclusive, at 288° to 330° C. (550° to 626° F.) with only 10 to 16.6 per cent loss in weight gave run resins with clean drip from the paddle but containing some spongy pieces of incompletely run resin. The Congos run at 344°, 357°, and 371° C. (651°, 675°, and 700° F.) were uniform thin liquids with a clean drip. Run 29 at 344° C. with only 11.7 per cent loss is exceptional and further work on it is intended. The changes in the appearance of the resin during running in closed kettles are similar to those in open kettles.

Closed Kettle Runs—20 Per Cent Loss in Weight

The maximum temperatures in these runs varied from 260° to 371° C. and the time at temperature from 15 minutes at 371° C. to 7 hours at 260° C. There were a few pieces of incompletely run resin at 260° C. All the other runs gave clean drip and oil soluble resins.

RUNNING CONGO RESIN

All of the runs discussed in each of the series above except those at temperatures below 260° C. and numbers 20, 21, 22, and 23, which contained a few pieces of incompletely run resin, produced oil soluble run Congos. Stable varnishes could have been made from each of them as soon as the running was complete by adding drying oils preheated enough to avoid chilling out the resin and cooking at the temperatures required by the oils used.

The open kettle method described in run No. 26 or a closed kettle run in which the Congo is held at 344° C. for about one hour, loses 17 to 20 per cent in weight, and passes through the physical changes described for run No. 26 would each yield run Congos usable for varnishes of any length up to 25 or 30 gallon. Though varnishes of greater length may be made from Congo, it does not show its best characteristics in long oil varnishes.

All of the above ways of running Congo are "single heat" methods. Some operators prefer to use a two or three heat method. In these the Congo may, for example, be heated to 330° C., let cool a few minutes, then reheated to 340° C., let cool a few minutes and then the running be completed at 352° C. By thus allowing intermediate cooling periods foaming is reduced and the cooling of the kettle walls permits an increased return of copal oil to the melt. Slack melts in which two or more natural resins are run together and many other variations are used to obtain special results. The running of natural resins is varied in many ways depending on the opinion and past experience of the operator and the results he wishes to produce. The same result may be obtained by different operators in very different ways. Natural resins have the great advantage, not generally possessed by synthetic resins, that the character of their varnishes may be adapted to the use for which they are intended, not only by the choice and handling of the oils and other materials used, but also by the manipulation of the resins themselves.

Physical and Chemical Properties of the Run Congos

(See Tables II and III and Charts 3 to 6 Inclusive)

The direct and indirect acid numbers of the original Hard Dark Amber Congo, of a commercially run Congo, and of each of the run resins were determined. The run Congos are soluble in the benzol-alcohol solution and give accurate acid numbers. The poor solubility of the original Congo makes its direct acid number vary considerably with the technique of the operator.

No consistently uniform relationship between the temperature at which the resin was run and the direct and indirect acid numbers is shown by the data.

The softening points were determined in capillary tubes, and the melting points by the mercury method of Rangiswami (Oil & Color Chemists Association, volume 13, page 287 (1930)). In this 0.2 gram of powdered resin is fixed to the bottom of a 17 cc. crucible by the gentlest possible warming. Fifty grams of mercury is added and a thermometer immersed in it. Heat at the first drop of resin comes to the surface. The greater hardness rate of 2° C. per minute and note the temperature at which the

of the run resins prepared in open kettles is indicated by their higher softening and melting points, as compared with those from closed kettles.

The solubilities were determined by rotating sealed wide mouth bottles containing equal weights of resin and solvent for 16 hours. In some cases the resin swelled and absorbed part or all of the solvent. If the bottle contained any liquid, the solubility of the resin was expressed:

S—Soluble—All the resin was in solution

PS—Partly soluble

I—Insoluble or only very small amounts in solution. If the resin had absorbed all of the solvent, swelling was only recorded; if the resin had absorbed part of the solvent, it was recorded as:

Sw—Swelled

PSw—Partly swelled.

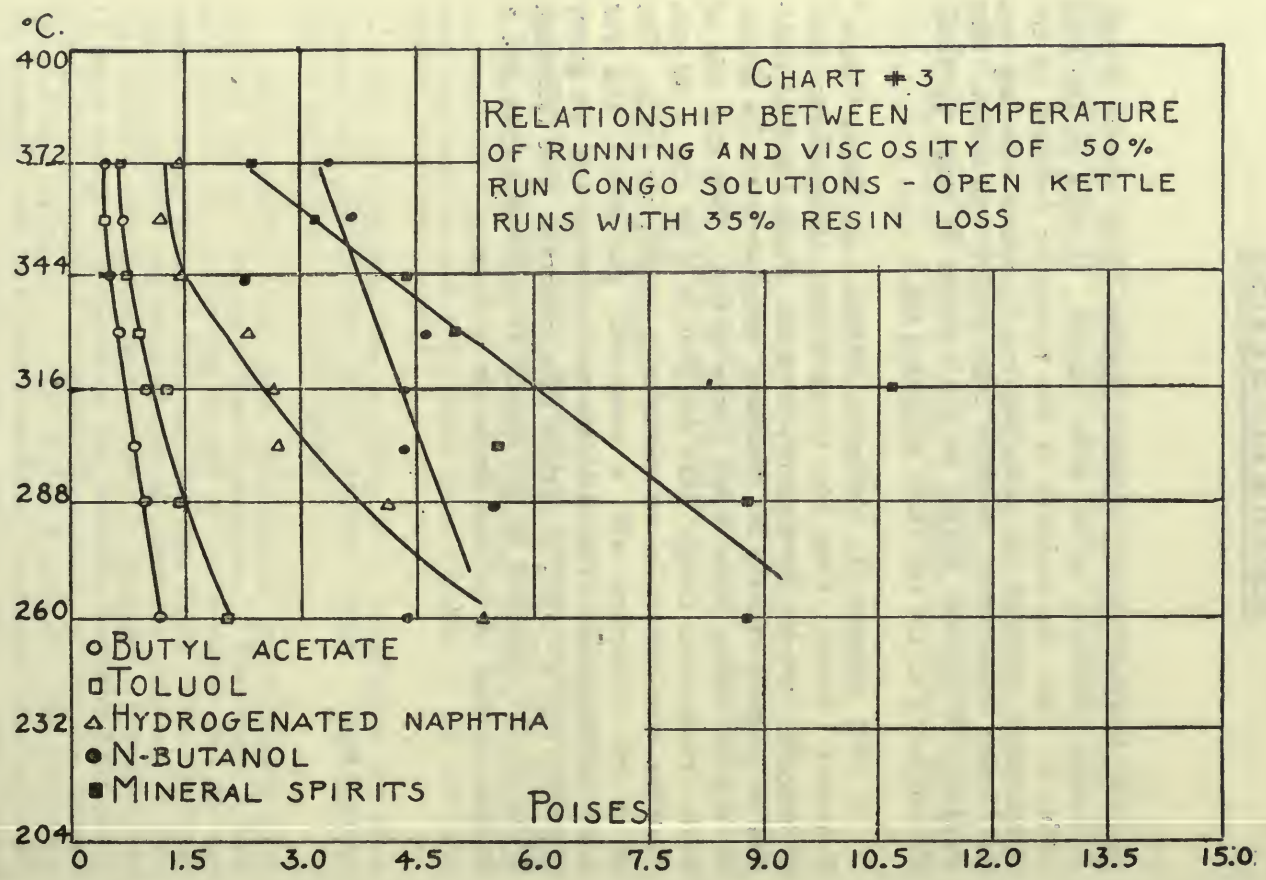
Each of the five solvents used represents one of the types in general use for either varnish or lacquer or both. Mineral spirits is a petroleum fraction distilling between 154° and 210° C. (309° and 410° F.). The hydrogenated naphtha used distills between 135° and 188° C. (275° and 370° F.). Toluol, butanol, and butyl acetate are extensively used solvents of the coal tar, alcohol, and ester types.

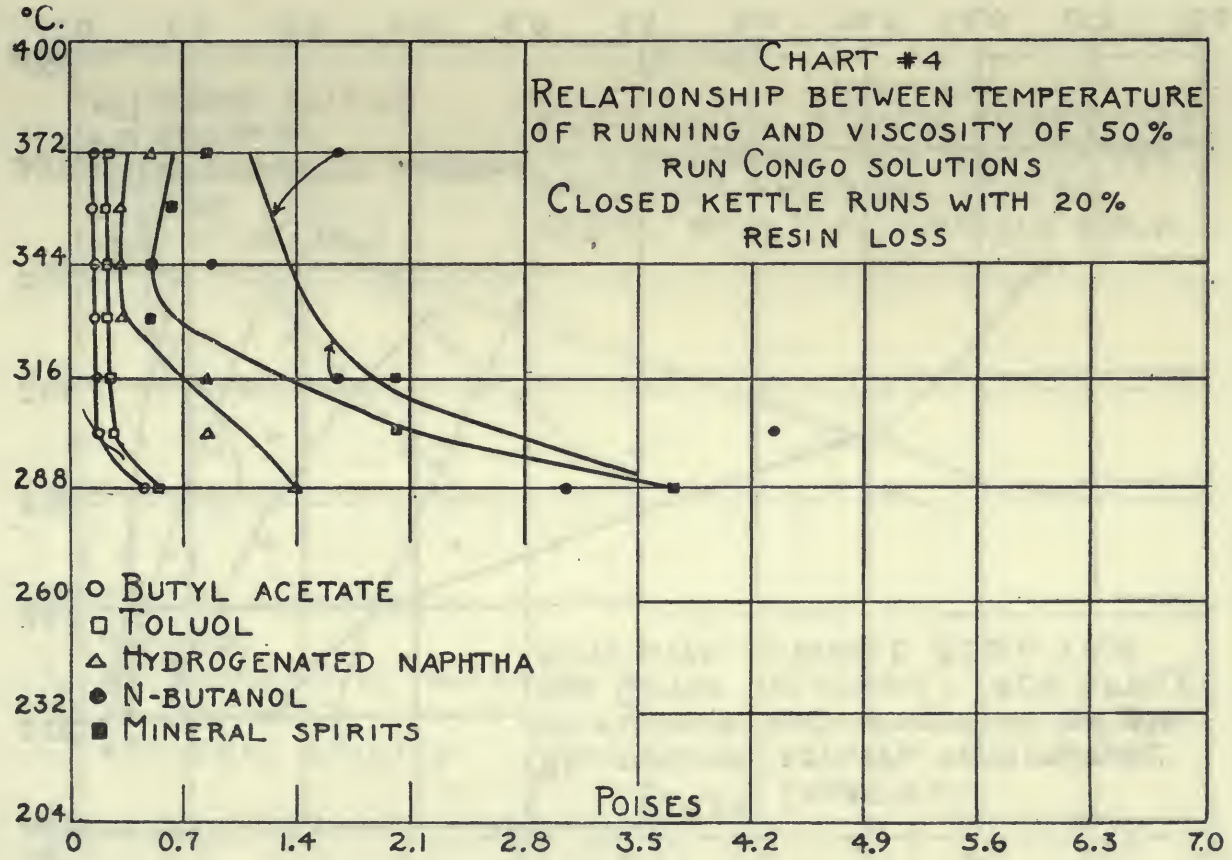
The viscosities of the solutions were determined by comparison with the Gardner-Holdt standard tubes. Their equivalent in poises is given in the charts.

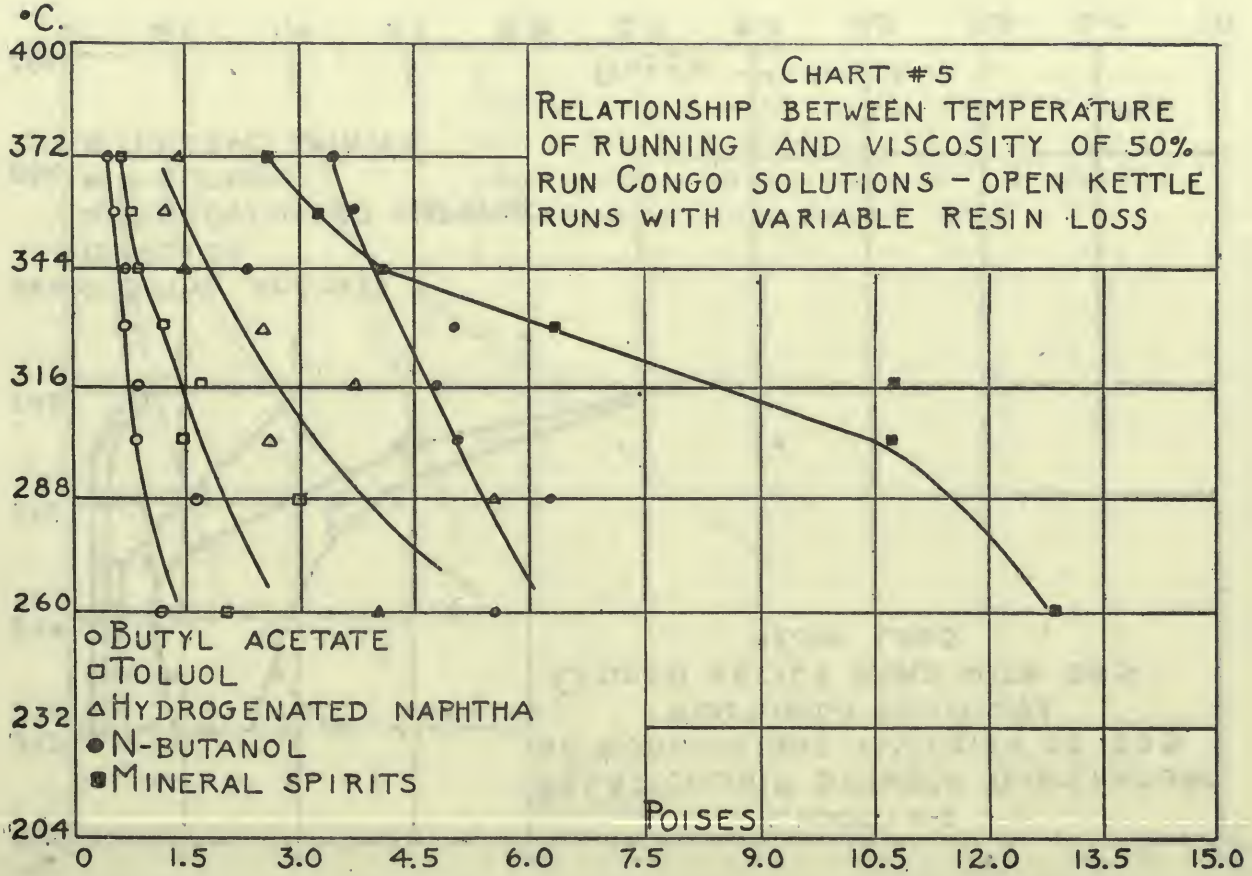
The solubility tests show conclusively the excellent solubility of the run Congos in the solvents used. Therefore, failure of a run Congo to dissolve in any of the solvents may be evidence of some unusual factor in the run resin. Run 40 shows low acid number and both 40 and 38 show low solvency in normal butanol. Further study of these is desirable. For solutions of equal strength, a relatively low viscosity indicates that either the dissolved material is especially soluble, or that the solvent is relatively stronger. In Charts 3 to 6, inclusive, the curves for the solvents, with very few exceptions, lie in the following order of increasing viscosity: butyl acetate, toluol, hydrogenated

naphtha, normal butanol, mineral spirits. Their solvent power, therefore, decreases in the order named. In each of the four series of runs, the majority of the viscosities decrease as the temperature at which the resin was run increases, showing that the higher temperatures produce more soluble run resins. The solubility in mineral spirits, to some extent at least, parallels the solubility of the run resin in linseed oil.

A 1935 bulletin (L. Hellinckx, "Studies on Copal Congo," Bruxelles Librairie Falk fils, Georges Van Campenhout, Successeur, 22, Rue des Paroissiens) from the Royal Colonial Institute of Belgium reports the results of some work on the chemical change taking place when Congo is run. Two kilo lots of white transparent Congo were distilled in a 50 cm. x 40 cm. stainless steel retort in an electrically heated air bath. The retort was connected with a condenser, gas meter, and gas analysis equipment. The distillate was collected and the gases measured and analyzed at various time intervals. The following tables give a summary of the results from several runs and a detailed account of the data from one of them.


°C.
400
372
344
316
288
260
232
204
CHART #3
RELATIONSHIP BETWEEN TEMPERATURE OF RUNNING AND VISCOSITY OF 50% RUN CONGO SOLUTIONS - OPEN KETTLE RUNS WITH 35% RESIN LOSS
BUTYL ACETATE
TOLUOL
HYDROGENATED NAPHTHA
N-BUTANOL
MINERAL SPIRITS
POISES
0
1.5
3.0
4.5
6.0
7.5
9.0
10.5
12.0
13.5
15.0


°C.
400
372
344
316
288
260
232
204
CHART #4
RELATIONSHIP BETWEEN TEMPERATURE OF RUNNING AND VISCOSITY OF 50% RUN CONGO SOLUTIONS
CLOSED KETTLE RUNS WITH 20% RESIN LOSS
BUTYL ACETATE
TOLUOL
HYDROGENATED NAPHTHA
N-BUTANOL
MINERAL SPIRITS
POISES
0
0.7
1.4
2.1
2.8
3.5
4.2
4.9
5.6
6.3
7.0


°C.
400
372
344
316
288
260
232
204
CHART #5
RELATIONSHIP BETWEEN TEMPERATURE OF RUNNING AND VISCOSITY OF 50% RUN CONGO SOLUTIONS – OPEN KETTLE RUNS WITH VARIABLE RESIN LOSS
○ BUTYL ACETATE
□ TOLUOL
△ HYDROGENATED NAPHTHA
● N-BUTANOL
■ MINERAL SPIRITS
POISES
0
1.5
3.0
4.5
6.0
7.5
9.0
10.5
12.0
13.5
15.0

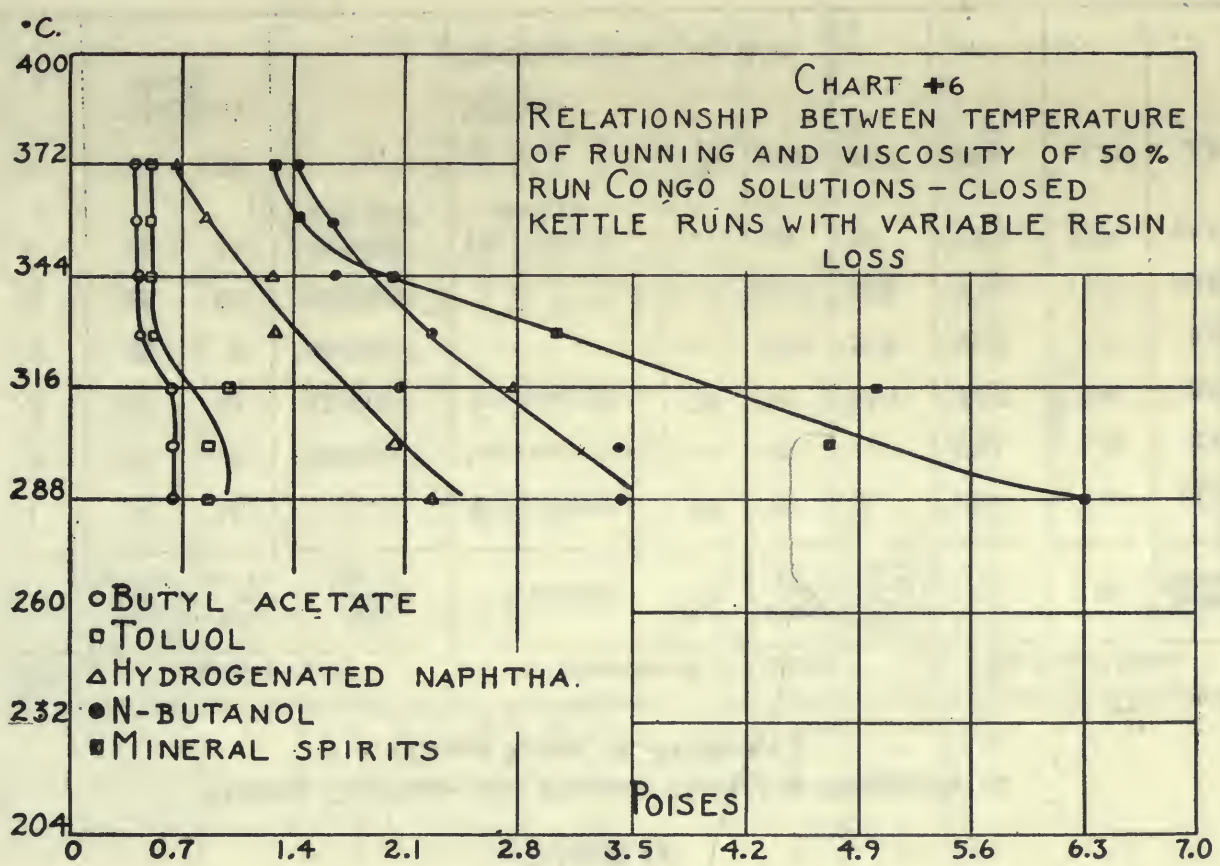

°C.
400
372
344
316
288
260
232
204
0
0.7
1.4
2.1
2.8
3.5
4.2
4.9
5.6
6.3
7.0
POISES
CHART #6
RELATIONSHIP BETWEEN TEMPERATURE OF RUNNING AND VISCOSITY OF 50% RUN CONGO SOLUTIONS – CLOSED KETTLE RUNS WITH VARIABLE RESIN LOSS
○ BUTYL ACETATE
□ TOLUOL
△ HYDROGENATED NAPHTHA.
● N-BUTANOL
■ MINERAL SPIRITS

TABLE IV.

Heating Conditions and Products Evolved in Distillation of Congo Resins. (L. Hellinckx.)

Run No.	Heating Rates			Properties of Run Resins				Gas Evolved Liters		
	Min. to Heat 300° C.	Min. at 300° C.	Min. above 300° C.	Appearance	M. P. °C.	Direct Acid No.	Per Cent Loss in wt.	CO_2	CO	Hydro Carbons
1	70	15	....	Yel. Brown...	59	38	..	39.8	5.4	16.6
2	130	40	50@310°	Incompl. run..	..	47	..	24.1	1.8	2.11
3	50	70	15@320°	Brown—yel. ..	79	51	12.1	43.8	5.0	3.7
4	60	0	80@370°		..	35.3	18.5	57.4	7.3	5.2
5	80	60	50@360°		..	42.4	16.5	50.4	5.9	10.3
6	90	60	30@350° 50@350°	Dk. Brown ... sticky.	..	40	20	49.3	11.0	16.5
7	90	70			79	80.8	10.7	35.4	1.17	1.59
	Original Resin			White—						
				Transparent ..	119	114	..	..	..	..

TABLE V.

Detailed Description of One Run (L. Hellinckx)

Time Minutes	Temp. °C.	Total gas evolved liters	Analysis of the Gas*				
			Per Cent CO_2	Per Cent CO	Per Cent Hydro-carbons	Per Cent CH_4	Per Cent H_2
15	115	4.70					
20	185	11.90					
30	188	16.60					
40	192	32.05					
45	202	33.50	70.0	0	0	14.0	16.0
55	270	57.00	79.6	1.8	0	8.8	9.7
60	270	62.60	89.0	2.4	2.0	4.0	2.6
70	296	87.50	88.0	5.0	2.3	2.7	2.3
75	305	97.60	85.0	12.1	5.3	4.7	4.0
80	315	103.30	56.0	21.5	8.1	8.6	5.9
85	280	109.20	35.7	12.2	18.3	19.6	14.0

*This analysis is for the gas evolved during the five minute interval ending at the stated time.

Hellinckx, as also have several other workers, concludes from a large amount of experimental and theoretical data that one of the most important reactions occurring during the running of Congo is the decomposition of dibasic acids to monobasic acids with evolution of carbon dioxide. He finds that the amount of carbon dioxide evolved is within 1.5 to 9 per cent of that calculated from the observed reduction in acid number, and that these reactions can be nearly or wholly completed at temperatures not above 310° C. At temperatures from 330° to 350° C.

and higher, alpha hydroxy acids break down to carbon monoxide and ketonic acids, monobasic acids break down to give hydrocarbons and carbon dioxide, and other reactions involving cracking and evolution of hydrocarbons occur. He found that at temperatures above 310° C. the reactions in general were detrimental to the quality of the resin. The following conclusions are translated directly from the pamphlet:

"Study of the running of Congo copal has showed that this operation has as its principal reaction the transformation of insoluble dicarboxylic acids into monocarboxylic acids soluble in drying oils.

"Other reactions can take place as well. The transformation of the oxy acid with loss of water and carbon monoxide, the decarboxylation of the monocarboxylic acids formed by the principal reaction into neutral bodies, as well as the phenomena of cracking; these secondary reactions are of small importance below 310° C., the temperature at which the principal reaction normally takes place.

"These considerations are very important in the technique of running. They show the importance of not passing the critical temperature of 310° C. When this temperature is passed, the secondary reactions assume a very great importance; these reactions are detrimental because they lead to a softer and more highly colored run copal and give varnishes of inferior quality and slow drying rate; further, they give rise to excessive losses."

Hellinckx does not give data showing the effect of temperatures above 310° C. on the solubility of the run Congo, nor does he indicate that *maximum* solubility has been reached at that temperature. Our curves show that a high degree of solubility may be obtained at temperatures below 310° C. They, however, also show numerous cases where greater solubility is obtained by running at higher temperature.

The higher original acid number of Hellinckx Congo, his considerably greater reduction in acid number of the run Congo, and his different conditions of running, prevent a ready correlation of the data.

Livache and McIntosh (Ach. Livache and John Geddes McIntosh, "The Manufacture of Varnishes and Kindred Indus-

tries," Scott, Greenwood & Son, London, 1908, volume II, page 96) give a table showing the increasing solubility of Congo in turpentine as the loss in weight on running increases. At 3 to 16 per cent, the run Congo is insoluble; at 20 to 22 per cent moderately soluble, and at 25 to 32 per cent it is very soluble.

Hellinckx's studies also show that Congo copal contains hydroyxl groups which can be readily esterified by a mixture of acetic acid and acetic anhydride. The resultant ester, the acetocopal, is a pale yellow transparent resin, soluble in benzol, toluol, amyl alcohol, amyl acetate, and benzyl alcohol, but less soluble in ethyl alcohol, carbon tetrachloride, ether and petrolic ether. It melts at 66° C. (151° F.), has an acid number of 121, a saponification value of 257, an iodine number of 129, and an index of refraction of 1.5267 at 20° C. Drying from a solution the acetocopal leaves a film of high gloss and good adhesive properties.

Perhaps the most interesting feature of the acetocopal is its compatibility with nitrocellulose and cellulose acetate. This new gum offers considerable promise as a resin for lacquers of all kinds.

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